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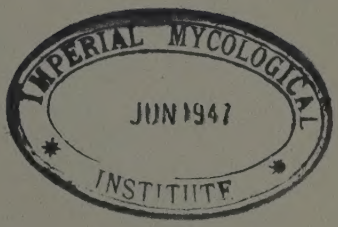

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MATHEMATICS

HOMOLOGICAL TRANSFORMATIONS OF FINSLERIAN METRIC

By V. WAGNER

(Communicated by A. N. Kolmogoroff, Member of the Academy, 17. XII. 1944)

As is known, the Finslerian metric is defined in the n-dimensional space X_n if at each point of X_n, in the tangent centro-affine Euclidean space E_n corresponding to this point there is given a certain hypersurface which, considered as the indicatrix, determines the Minkowskian metric in E_n (1). Thus, the geometry of Finslerian space is equivalent to the geometry of field of local hypersurfaces in X_n.

Let

$$x^a = l^a(\xi^\omega, \eta^l), \quad y_a = l_a(\xi^\omega, \eta^l) \tag{1}$$
$$\alpha, \beta, \ldots, \omega = 1 \ldots n, \quad a, b, \ldots, l = 1 \ldots n-1$$

be the equations of the indicatrices of Finslerian space F_n in the point coordinates x^a and in the hyperplane coordinates y_a, respectively, where ξ^ω are the coordinates of the corresponding point in F_n.

The fundamental differential equations of centro-affine geometry of hypersurfaces

$$\left.\begin{aligned} &{}^1\nabla_c\, l^a_b = \partial_c\, l^a_b - {}^1G^l_{cb}\, l^a_l = -g_{cb} l^a \\ &{}^2\nabla_c\, l_{b\alpha} = \partial_c\, l_{b\alpha} - {}^2G^l_{cb}\, l_{l\alpha} = -g_{cb} l_\alpha \\ &\partial_c = \frac{\partial}{\partial \eta^c}, \quad l^a_b = \partial_b l^a, \quad l_{b\alpha} = \partial_b l_\alpha \end{aligned}\right\} \tag{2}$$

define two projectively flat linear affine connexions with the coefficients ${}^1G^l_{cb}$ and ${}^2G^l_{cb}$ which are conjugated with respect to the tensor g_{cb} (2):

$${}^1\nabla_d g_{cb} = -{}^2\nabla_d\, g_{cb} = 2A_{dcb} \tag{3}$$

where A_{dcb} is a tensor. The tensor g_{cb} determines the angular quadratic form of F_n. We shall use g_{cb} for raising and lowering the indices.

We have

$${}^1G^a_{cb} - {}^2G^a_{cb} = 2A^{\cdots a}_{cb} \tag{4}$$

Consider the homological transformations in the tangent E_n determined by the equations in the point coordinates and hyperplane coordinates, respectively:

$${}'x^a = \frac{x^a}{1 - \sigma_\beta x^\beta}, \quad {}'y_a = y_a - \sigma_a \tag{5}$$

where $\sigma_\alpha = \partial_\alpha \sigma$ is the gradient of a scalar function σ in F_n.

The transformation (5) transforms each indicatrix into a certain hypersurface. These hypersurfaces taken as indicatrices determine a new Finslerian metric. It can be shown that the curves of the extremal length of the arc are preserved under this homological transformation of Finslerian metric (3).

Let g_{cb} determine a positive definite quadratic form, which means that the indicatrices are convex. Now we suppose that the hyperplane σ_α which under the transformation (5) transforms into the hyperplane at infinity, is a tangent hyperplane of the indicatrix. In this case the scalar $\sigma = \sigma(\xi^\omega)$ must be a solution of the Pfaffian equation

$$d\sigma = l \tag{6}$$

where $l = l_a\, d\xi^a$.

The direction of the radius-vector of the contact point of σ_α will be an isotropic direction of the transformed Finslerian metric. Thus, we obtain a congruence of isotropic curves which are obviously the extremals with respect to the transformed metric, and therefore they are the extremals with respect to the initial metric.

Denoting by $[dl]$ the Cartan exterior differential of the Pfaffian form l, we put:

$$[dl] = \Lambda^{cb}\,[l_c l_b] + \Lambda^b\,[l l_b] + [d\eta^b l_b] \tag{7}$$

where $l_b = \partial_b l$ and the brackets mean the Cartan exterior multiplication of Pfaffians. According to (7), the characteristics of the Pfaffian equation (6) are determined by the equations

$$\frac{d\xi^a}{ds} = l^a(\xi^\omega, \eta^l), \quad \frac{d\eta^a}{ds} + \Lambda^a = 0 \tag{8}$$

In X_n these equations determine the curves which can be made isotropic by the suitable homological transformation of the Finslerian metric, and therefore the equations (8) are the differential equations of the extremals. What had been said above gives a geometric interpretation of the well-known Carathéodory method in the calculus of variations ([3]). It follows that from the point of view of calculus of variations it is very interesting to study the properties of Finslerian space, which are invariant under the homological transformation of metric. The theory of hypersurfaces in the central E_n, subjected to arbitrary transformations (5), is equivalent to the theory of hypersurfaces in the centro-projective space. It can be shown that the coefficients of affine connexions

$$\overset{1}{*}\Gamma^a_{cb} = \overset{1}{\Gamma}{}^a_{cb} + \frac{1}{n+1}\delta^a_{(c}A_{b)}, \quad \overset{2}{*}\Gamma^a_{cb} = \overset{2}{\Gamma}{}^a_{cb} - \frac{2}{n+1}A^a g_{cb} \tag{9}$$

where $A_b = \overset{\cdot\cdot}{A}{}^c_{bc}$, are invariant under the transformations (5), and therefore the affinor

$$\overset{\cdot\cdot}{P}{}^a_{cb} = \frac{1}{2}(\overset{2}{*}\Gamma^a_{cb} - \overset{1}{*}\Gamma^a_{cb}) = \overset{\cdot\cdot}{A}{}^a_{cb} - \frac{1}{n+1}(2\delta^a_{(c}A_{b)} + g_{cb}A^a) \tag{10}$$

is also invariant. The vanishing of $\overset{\cdot\cdot}{P}{}^a_{cb}$ characterizes the hyperquadrics. Leaving them out of consideration we can suppose the scalar

$$I = \overset{\cdot\cdot}{P}{}^a_{cb}\,\overset{\cdot\cdot}{P}{}^b_{da}\,g^{cd} \tag{11}$$

to be different from zero because g_{cb} determines a definite quadratic form. By means of this scalar we define the invariant tensor

$$a_{cb} = I g_{cb} \tag{12}$$

Let us consider the indicatrices of F_n as local $n-1$-dimensional spaces X_{n-1}'s of the compound manifold $X_{n+(n-1)}$([4]) whose basic space is the space F_n itself. We introduce a linear connexion in this $X_{n+(n-1)}$ by means of the equation

$$\delta\eta = d\eta^a + \Gamma^a = 0 \tag{13}$$

where $\Gamma^\alpha = \Gamma^\alpha_\alpha(\xi^\omega, \eta^l)\, d\xi^\alpha$ are the given Pfaffians determining the connexion.

Every linear connexion in $X_{n+(n-1)}$ determining the mapping of the indicatrices one onto another thus determines a parallel displacement of vectors in F_n, and inversely. It can be shown that the connexion in $X_{n+(n-1)}$ corresponding to the Berwald parallel displacement of vectors in F^n [1] is defined by the following two conditions:

$$\left.\begin{aligned} [Dl] &= [d\xi^\alpha \partial_\alpha l] - [\Gamma^\alpha l_\alpha] = 0 \\ D_0 g_{cb} &= l^\alpha D_\alpha g_{cb} = 0 \end{aligned}\right\} \tag{14}$$

The first of these conditions is that the exterior covariant differential $[Dl]$ of the Pfaffian l vanishes. This means geometrically that the extremals coincide with the geodesics, and that the first curvature affinor of hypersurfaces in F_n is symmetric. The second condition means that the infinitesimally small angles between the geodesics and the parallelly displaced directions along these geodesics are constant.

From (14) we obtain the explicit expression for Γ^α:

$$\Gamma^\alpha = \left\{ \Lambda^{ba} + \frac{1}{2}\left(l^\alpha \partial_\alpha g^{ba} - \Lambda^c \partial_c g^{ba} + \partial_c \Lambda^a g^{cb} + \partial_c \Lambda^b g^{ca}\right) \right\} l_b + \Lambda^a l \tag{15}$$

A necessary and sufficient condition that F_n be a Minkowskian space is that the connexion (15) be of zero curvature, and $\overset{2}{G}{}^a_{cb}$ or, what is the same, $\overset{1}{G}{}^a_{cb}$ determine a constant field in $X_{n+(n-1)}$.

Since the first equatian of (14) is invariant under the homological transformations (5), we obtain a linear connexion in $X_{n+(n-1)}$ which will be invariant under these transformations if we replace the second of the equations (14) by the following invariant equation

$$D_0 a_{cb} = 0 \tag{16}$$

Denoting by $^*\Gamma^\alpha$ the Pfaffians determining this connexion, we have

$$^*\Gamma^\alpha = \Gamma^\alpha - \frac{I'\partial_\alpha I - \Lambda^c \partial_c I}{2I} g^{ba} l_b \tag{17}$$

The necessary and sufficient condition for F_n to be transformed into a Minkowskian space by means of a homological transformation (5) is that the connexion (17) be of zero curvature, and that a_{cb} and $^*\overset{2}{G}{}^a_{cb}$ or, what is the same, $^*\overset{1}{G}{}^a_{cb}$ determine constant fields in $X_{n+(n-1)}$.

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MATHEMATICAL PHYSICS

SOLUTIONS OF VECTOR BOUNDARY PROBLEMS OF MATHEMATICAL PHYSICS FOR THE SPHERE

By G. I. PETRASHEN

(Communicated by V. I. Smirnov, Member of the Academy, 20. III. 1944)

We construct a system of vector-functions for spherical domains which is called a system of spherical vectors. By using it the solution of vector problems in mathematical physics is reduced to the solution of similar scalar problems if only the latter is required to have the form of a series of spherical functions.

1. Let $Y_{lm}(\vartheta, \varphi)$ be the usual system of not normed spherical functions.

By spherical vectors we shall call the following family of linearly independent vectors:

$$\left.\begin{aligned} \mathbf{Y}^0_{lm} &= [\mathbf{r}\ \operatorname{grad} Y_{lm}(\vartheta,\varphi)] \quad (l=1,2,\ldots) \\ \mathbf{Y}^{+1}_{lm} &= (l+1)\,\mathbf{r}\,Y_{lm}(\vartheta,\varphi) - r\ \operatorname{grad} Y_{lm}(\vartheta,\varphi) \quad (l=0,1,2,\ldots) \\ \mathbf{Y}^{-1}_{lm} &= l\,\mathbf{r}\,Y_{lm}(\vartheta,\varphi) + r\ \operatorname{grad} Y_{lm}(\vartheta,\varphi) \quad (l=1,2,\ldots) \end{aligned}\right\} \tag{1}$$

The spherical vectors $\mathbf{Y}^{\nu}_{lm}(\vartheta, \varphi)$ whose index ν has the values $0, +1$ or -1 possess the following properties:

a) The orthogonality property on the sphere (ϑ, φ):

$$\int ({}_0\mathbf{Y}^{\nu}_{lm}\ {}_0\mathbf{Y}^{\nu_1}_{l_1 m_1})\, d\Omega = 0 \tag{2}$$

if (ν, l, m) and (ν_1, l_1, m_1) differ from each other in at least one index.

b) The possibility of approximation of an arbitrary vector-function $\mathbf{U}(\vartheta, \varphi)$ by the series

$$\mathbf{U} = \sum_{\substack{l=0 \\ |m|<l}}^{\infty} a^0_{lm}\mathbf{Y}^0_{lm}(\vartheta,\varphi) + a^{+1}_{lm}\mathbf{Y}^{+1}_{lm}(\vartheta,\varphi) + a^{-1}_{lm}\mathbf{Y}^{-1}_{lm}(\vartheta,\varphi) \tag{3}$$

c) The property to yield a vectorial harmonic polynomial of order $l+\nu$ by means of multiplication of the spherical vector $\mathbf{Y}^{\nu}_{lm}$ by $r^{l+\nu}$. This latter property may be taken for the definition of the family (1).

2. Problems often arise in which a vector $\mathbf{U}$ is to be represented as a sum of a potential and a solenoidal vector, *i. e.* $\mathbf{U} = \mathbf{U}_1 + \mathbf{U}_2$, where rot $\mathbf{U}_1 = 0$ and div $\mathbf{U}_2 = 0$.

Applying the operation div and rot to the (lm)-th term of the decomposition (3) of a potential vector, we obtain

$$\mathbf{U}_1 = \sum_{\substack{l=0 \\ |m|<l}}^{\infty} \Phi^{+1}_{lm}(r,t)\,\mathbf{Y}^{+1}_{lm} + \Phi^{-1}_{lm}(r,t)\,\mathbf{Y}^{-1}_{lm} \tag{4}$$

where the functions Φ_{lm}^{+1} and Φ_{lm}^{-1} are connected by the following relation:

$$\frac{\partial \Phi^{-1}}{\partial r} - \frac{l-1}{r}\Phi^{-1} = \frac{\partial \Phi^{+1}}{\partial r} + \frac{l+2}{r}\Phi^{+1}. \tag{5}$$

Similarly the representation of a solenoidal vector has the form

$$\mathbf{U} = \sum_{\substack{l \geqslant 0 \\ |m| \leqslant l}}^{\infty} \varphi_{lm}^{0}(r,t)\,\mathbf{Y}_{lm}^{0} + f_{lm}^{+1}(r,t)\,\mathbf{Y}_{lm}^{+1} + f_{lm}^{-1}(r,t)\,\mathbf{Y}_{lm}^{-1} \tag{6}$$

where φ_{lm}^{0} is arbitrary, and the functions f_{lm}^{+1} and f_{lm}^{-1} are subjected to the condition

$$(l+1)\left(\frac{\partial f^{+1}}{\partial r} + \frac{l+2}{r} f^{+1}\right) + l\left(\frac{\partial f^{-1}}{\partial r} - \frac{l-1}{r} f^{-1}\right) = 0 \tag{7}$$

The representation of the vector $\mathbf{U}$ in the form of the sum of vectors (4) and (6) is unique up to a Laplacian vector.

3. Consider the solution of the wave equation

$$\Delta \mathbf{U} - c^2 \frac{\partial^2 \mathbf{U}}{\partial t^2} = 0 \tag{8}$$

for the sphere $0 \leqslant r \leqslant R$ under the initial conditions

$$\mathbf{U}\Big|_{t=0} = \frac{\partial \mathbf{U}}{\partial t}\Big|_{t=0+0} = 0 \tag{9}$$

and the simplest boundary conditions

$$\mathbf{U}\,|_{r=R} = \mathbf{U}_0(\vartheta, \varphi, t) \tag{10}$$

A vector $\mathbf{U}_0$ defined on the surface of the sphere is representable in the form of a series of spherical vectors

$$\mathbf{U}_0 = \sum_{\substack{l=0 \\ |m| \leqslant l}}^{\infty} \alpha_{lm}^{0}(t)\,\mathbf{Y}_{lm}^{0} + \alpha_{lm}^{+1}(t)\,\mathbf{Y}_{lm}^{+1} + \alpha_{lm}^{-1}(t)\,\mathbf{Y}_{lm}^{-1} \tag{11}$$

and we are now to look for the solution of the problem in the form of a series (3).

Substituting (3) into the equation (8) as well as into the conditions (9) and (10), we arrive at the problem of integrating the equations

$$\frac{\partial^2 \varphi_n}{\partial r^2} + \frac{2}{r}\frac{\partial \varphi_n}{\partial r} - \frac{n(n+1)}{r^2}\varphi_n = c^2 \frac{\partial^2 \varphi}{\partial t^2} \qquad (n = l + \nu) \tag{12}$$

in the interval $0 \leqslant r \leqslant R$ for $t \geqslant 0$ under the initial conditions

$$\varphi_n(r,t)\Big|_{t=0} = \frac{\partial \varphi_n}{\partial t}\Big|_{t=0+0} = 0 \tag{13}$$

and the following boundary conditions:

$$\varphi_n(R,t) = a(t) \tag{14}$$

4. We determine a class of continuous solutions of the equation (12) in the interval $0 \leqslant r \leqslant R$ valid for all times $t \geqslant 0$ assuming that the boundary conditions are subjected to the condition of smoothness, *i. e.* that

1°. $a(t)$ and $a'(t)$ are continuous and vanish for $t = 0$.

2°. $a''(t)$ is piecewise continuous.

Generalizing the method proposed by Smirnov [1], it is natural to look for a solution in the form

$$\varphi_n(r,t) = \int_0^{t-cr} \omega_{1n}(\tau)\, Q_{n+1}\left(\frac{t-\tau}{cr}\right) d\tau + \int_0^{t-cR+cr} \omega_n(\tau)\, Q_{n+1}\left(\frac{r+cR-t}{cr}\right) d\tau$$

choosing ω_{1n} and ω_n such that the solution should be a finite one for $r=0$. Using the symmetry properties of the functions $Q_{n+1}(x)$ it is easily seen that this condition is satisfied if and only if

$$\omega_{1n}(\tau)=0 \text{ for } \tau<cR$$

and

$$\omega_{12\nu}(\tau+cR)=\omega_{2\nu}(\tau),\ \omega_{12\nu+1}(\tau+cR)=-\omega_{2\nu+1}(\tau)$$

$\nu\geqslant 0$, which expresses the law of reflection of disturbances from the origin. The required solution is then represented by the formulae

$$\left.\begin{aligned}\varphi_0(r,t)&=\int_{t-cR-cr}^{t-cR+cr}\omega_0(\tau)\left(\frac{\tau+cR-t}{cr}-1\right)d\tau+2\int_0^{t-cR-cr}\omega_0(\tau)\,d\tau\\ \text{for } n=0 \text{ and}&\\ \varphi_n(r,t)&=\int_{t-cR-cr}^{t-cR+cr}\omega_n(\tau)\,Q_{n+1}\left(\frac{\tau+cR-t}{cr}\right)d\tau\end{aligned}\right\}\qquad(15)$$

for $n\geqslant 1$.

By direct differentiation we may verify that the solutions (15) satisfy the equation (12) for any piecewise continuous $\omega_n(\tau)$ and satisfy the initial conditions if $\omega_n(\tau)=0$ for $\tau<0$.

These solutions are continuous together with their first derivatives for $r\geqslant\varepsilon>0$. At the point $r=0$ all $\varphi_n=0$ if $n\geqslant 1$, and are finite for $n=0$; the first derivatives are bounded for all times $t>0$ in the neighbourhood of this point, and for $n\geqslant 2$ these derivatives are always equal to zero, except for some definite moments of time.

It is easily established that under the conditions indicated the solution of the problem is unique.

5. In order that (15) should be the solution of the problem, it is necessary to determine the functions $\omega_n(\tau)$ for $\tau\geqslant 0$ from the boundary conditions (14) which in the case $n\geqslant 1$ assume the following form:

$$\omega_n(t)-(-1)^n\omega_n(t-t_0)-\frac{1}{cR}\int_{t-t_0}^{t}\omega_n(t)\,P_n'\left(\frac{\tau+cR-t}{cR}\right)d\tau=-cRa''(t)\qquad(16)$$

where $t_0=2cR$.

Representing an arbitrary moment of time t in the form of the sum $t=t'+qt_0$, where q is an integer and t' lies in the interval $0\leqslant t'\leqslant t_0$, we introduce the following notations:

$$\omega_n(t'+qt_0)=\tilde{\omega}_q(t'),\qquad -cRa''(t'+qt_0)=\varphi_q(t')\qquad(17)$$

Then

$$\tilde{\omega}_q(t')-\frac{1}{cR}\int_0^{t'}\tilde{\omega}_q(\tau)\,P_n'\left(\frac{\tau+cR-t'}{cR}\right)d\tau=\Phi_{q-1}(t')\qquad(18)$$

where the function $\Phi_{q-1}(t')$ has the following value:

$$\Phi_{q-1}(t')=\varphi_q(t')+(-1)^n\tilde{\omega}_{q-1}(t')+\frac{1}{cR}\int_{t'}^{t_0}\tilde{\omega}_{q-1}(\tau)\,P_n'\left(\frac{\tau+cR-t'-t_0}{cR}\right)d\tau\qquad(19)$$

For $q=0$ the right-hand side of the equation (18) is known and, consequently, the function $\tilde{\omega}_0(t')$ may be determined by the usual methods of integration of Volterra equations of the second kind with a kernel depending on the difference.

The so obtained function $\omega_0(t')$ determines $\Phi_0(t')$, which enables us to find $\tilde{\omega}_1(t')$; this function, in its turn, determines $\Phi_1(t')$, *etc.*

Thus, for the solution of the problem we have to find the resolvent $R(r-t')$ of the kernel $-\frac{1}{cR}P_n'\left(\frac{\tau+cR-t'}{cR}\right)$, and apply the method of successive approximations.

6. It is possible to construct the solutions of the equation (12) under less restricting assumptions with respect to the boundary functions $a(t)$ from (14).

We shall assume that $a(t)$ is continuous for $t \geqslant 0$, vanishes for $t=0$ and possesses a piecewise continuous derivative such that $a'(0)$ is not necessarily zero.

The functions

$$\psi_n(r,t) = -\frac{1}{cr}\int_{t-cR-cr}^{t-cR+cr} \omega_n(\tau)\, P_n\left(\frac{\tau+cR-t}{cr}\right)d\tau \qquad (20)$$

obtained by differentiating with respect to t the solutions (15), evidently also satisfy the equation (12) for arbitrary piecewise continuous $\omega_n(\tau)$ satisfying the zero initial conditions, if $\omega_n(\tau)=0$ for $\tau<0$, and may also satisfy the boundary conditions with discontinuities in the first derivatives, if the functions $\omega_n(\tau)$ are determined in the same way as in n°5. In the case of a continuous $\omega_n(\tau)$ satisfying the condition $\omega_n(0)=0$ and differentiable, these solutions belong to the class (15).

It may be easily established that the family of functions (20) represents the solutions of the equation (12) with regular strong discontinuities on the characteristics. They remain finite at the origin and their derivatives have poles of an order not higher than one.

In view of these facts the uniqueness theorem remains valid.

The Leningrad Academy
of Air Forces of the Red Army.

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PHYSICS

A NEW VARIETY OF ALKALI-HALIDE PHOSPHORS

By F. D. CLEMENT

(Communicated by A. N. Terenin, Member of the Academy, 31. V. 1944)

In a previous communication (1) A. N. Terenin reported having observed fluorescence of alkali-halide salts coated with certain metals by evaporation in a vacuum. In this report we present some of the results of a further study of this phenomenon which has formed a basis for the development of a method of producing a new variety of phosphors.

In general terms the essence of the method may be described as follows. One of the branches of a quartz test-tube with two branches is loaded with the alkali-halide salt which is the base of the phosphor, and the other branch, with a substance which acts as the activator. The test-tube is connected to a vacuum pump and evacuated, being kept at a temperature of 200—300° C for about one half hour. After this, the evacuation being continued, the test-tube is cooled, and a little electric furnace is fitted on to the branch containing the alkali-halide salt. When the temperature of the branch reaches about 700° C, the salt begins to volatilize and forms a molecular current which condenses upon the cold walls of the test-tube or upon a special screen, forming a thin layer of fine crystalline structure. Then the second branch is heated, which causes a very fine sublimate of activator to form on the salt layer. The system produced in this manner (base + activator) is, depending on the composition of the components, either the finished phosphor, or it requires some further treatment, which will be described below.

The main technical feature of this method is the fact that the phosphor is produced in the form of a ready-made fluorescent screen with very good structural and technical properties. Sublimating the salt under vacuum gives dense, even layers with fine even-sized crystals, firmly fastened to the ground. The thickness of the layer can be regulated within a wide range—from extremely fine, absolutely transparent layers which can be detected only by their interference colouring, up to several tenths of a millimeter. The size of the single crystals making up the layer is of the order of 1 μ and varies according to the temperature of the ground during sublimation.

Since phosphors are used in practice chiefly in the form of screens, and the methods of preparing these latter do not as yet meet all requirements (particularly, screens have not been able to be imparted rarefying properties), the properties mentioned of our phosphors should hold considerable technical interest. However, during our study it was found that phosphors produced by sublimation differed in some of their properties from otherwise produced phosphors of identical composition, *e. g.* Pohl's single crystal phosphors (2). For this reason we have grouped them into a separate variety and have called them «sublimate-phosphors».

First of all, we made an elaborate study of the conditions under which sublimate-phosphors can be produced. It was found that sublimate-phosphors of various

composition are produced with varying degrees of difficulty. In some cases sublimation of the activator on to the base-layer immediately gave the finished phosphor, while in others the system produced in this manner became a phosphor only after some time, and still in others it was necessary to heat the layer at a definite temperature, different for different substances. It was suggested that during the formation of the phosphor, activator molecules probably diffused into the lattice of the base, and that the various times or heats required to make the system a phosphor probably depended on various diffusibilities due to various sizes of the diffusing molecules and various lattice constants: the weaker the bond between the component elements of the base lattice and the smaller the activator molecules, the easier and faster diffusion should proceed.

In order to check this assumption a systematic study was made. First of all, the activator being kept constant (TlCl) we changed the alkali-halide bases so as to vary their lattice constants. Here are the results for various chlorides:

Phosphor base	LiCl	NaCl	KCl	RbCl	CsCl
Temperature required in °C	—	200—250	100—110	80—90	50—60
Lattice constant in Å	2.57	2.81	3.14	3.27	3.63

With LiCl which has the lowest lattice constant as base, the phosphor did not form even when the layer was heated to a temperature of 500—600° C, at which temperature the activator had completely volatilized away from the layer. In the case of CsCl after standing for a few hours the layer CsCl + TlCl turned into a phosphor without heating, *i. e.* at room temperature. These data show that in accordance with our assumption, the temperature required drops with an increase of the lattice constants.

After this, having the base (KCl) constant, we tried activators with varying molecule dimensions but with otherwise similar chemical and physical properties. For this purpose we used various thallium halides whose molecule sizes increase from TlCl to TlI. The results were as folow

Activator	TlCl	TlBr	TlI
Temperature required in °C	100—110	150—200	~400

It is easy to see that these data also confirm our assumption.

Since only free particles, of course, can diffuse, and since in order to attain a definite concentration of these, *i. e.* a definite vapour tension of the gaseous phase of the activator in the sublimated layer, the less the volatility of the activator, the higher the temperature required, it may be thought that this might be the cause of the observed relationship (the volatility of the salts used decreases in the following order TlCl → TlBr → TlI).

However, within the temperature range of these experiments, the temperature of TlI has to be only 25° higher than that of TlCl for their vapour tensions to be equal.

Besides, unlike the first series of observations, in this latter case the base and the activator had different anions. It may be thought that the phosphor formed with greater difficulty on account of this. For this reason another experiment was set up. TlCl was sublimated as activator on to KI. In this system the anions differ also, but, at the same time, KI's lattice constant (3.53 Å) is very close to that of CsCl. The temperature required to turn this system into a phosphor was found to be ≃ 60° C (the temperature for CsCl is 50—60°!). And in this case, just as in that of the system CsCl + TlCl, the system attained luminescent properties after a few hours' standing without heating.

Finally, we tried CsI as a base, the latter having the highest lattice constant (3.95 Å) of all alkali-halide salts. Just as was to be expected according to our assump-

tion, CsI with TlCl as the activator formed a phosphor immediately upon sublimation without any additional heating (in spite of the difference in anions). Such thallium salts as $TlNO_3$ and Tl_2S were tried as activator, as well as metallic thallium which was used in all the first experiments. These substances also form bright phosphors with alkali-halide bases but, as might have been expected, phosphors with $TlNO_3$ form with greater difficulty than with TlCl (with Tl_2S, with still greater difficulty). Phosphors with metallic Tl form with somewhat more difficulty than with TlCl, which is probaby due to the much lower volatility of Tl.

Besides Tl, a whole series of metals and various halide salts of these metals were tested as activators (*viz.* Cu, Ag, Au, Ca, Zn, Cd, Hg, Ga, Sn, Pb, Bi)—about 30 systems in all. With the exception of HgCl in KCl, all these substances, as a rule, formed much duller phosphors than thallium. In some cases the luminescence was just within the range of visibility ($MgCl_2$, Sn and $BiCl_2$ in KCl), some systems did not give phosphors with visible luminescence (Ca, Ga, Pb, Bi in NaCl, Zn in NaI, Cd in KCl, Bi in KCl, CsCl, NaBr). But in all comparable cases, *i. e.* in those cases where within the series only one parameter was varied, *e. g.* only the phosphor base, or only the anion or cation of the activator (in the case last mentioned only chemically related cations were compared), the conclusions drawn for thallium phosphors were fully confirmed. Time and heat facilitate phosphor formation in all cases. The higher the lattice constant, the easier the phosphor forms; and the larger the activator molecule or the lower its volatility, the greater the difficulty of phosphor formation. In particular, when the activators are metals, the phosphors form with greater difficulty than when the more volatile salts of these metals are used (Zn, Hg, Pb, Bi, Sn).

In view of all these data we consider it possible to assert that sublimate-phosphors are not of a purely surfacial (adsorptional) nature, since during the formation of sublimate-phosphors the activator really diffuses through the lattice of the base to some depth, whereas the function of thermal treatment is to facilitate this diffusion. However, in view of a whole series of additional data, concerning spectral properties, optimum concentration and the duration of luminescence of the sublimate-phosphor, we are of the opinion that for most activators this diffusion takes place within a very shallow zone close to the surfaces of the base crystals. At the same time our assumption implies that penetration of the base lattice by the activator is essential only as a necessary preliminary condition for those processes which consequently take place within the lattice and result in the formation of luminescence «centres», and the nature of which we do not attempt to explain in our statement. Moreover, we have unquestionable evidence to the effect that the conditions necessary for the appearance of luminescent properties are by no means exhausted by the conditions of diffusion of the activator into the base, and certain other properties are essential in the component substances which form the phosphor. Thus, although Cd has a smaller atomic radius than Tl and is more volatile, the former does not form a phosphor with HCl, whereas the latter gives excellent luminescence.

Neither can differences in luminescent intensities of alkali-halide phosphors with various activators be explained only by the conditions of diffusion of the activator into the base.

Our conceptions of the diffusion of the activator into the alkali-halide base are in full accordance with the views of Tiede and his collaborators on the nature of the processes of phosphor formation ([3]), and with Riehl's experiments ([4]) on the diffusion of Cu in ZnS.

The conclusion that heating the system «base + activator» is necessary only in order to facilitate the diffusion of the activator into the base, *i. e.* is connected with a definite aggregate state of the phosphor component, suggested varying the method of volatilization. Indeed, if both components of the phosphor are mixed in the course of volatilization, while yet in the gaseous phase, when they are in a molecular state of dispersion, the activator particles upon sublimation should «intercrystallize» with the substance of the base, which should eliminate all necessity of diffusion and, therefore, of heating. We tried volatilizing the base

and the activator simultaneously, and found, as was expected, that no additional heating was necessary. In this case the layer was already a phosphor immediately after sublimation even for those substances which required additional heating to a high temperature when the substances were volatilized separately. Moreover, upon simultaneous volatilization in some cases phosphors formed from substances in which diffusion had not taken place even at high temperatures, and which had, therefore, not given phosphors at all when volatilized separately (*e. g.* NaCl + Pb). This makes it possible to explain the fact that for certain activators (Ag. Pb, *etc.*) the method of separate volatilization gives duller alkali-halide phosphors than when the same phosphors are prepared from a melt (the activator having difficulty in diffusing into the base from outside).

A more elaborate spectrum analysis of sublimate-phosphors than was reported in paper (1) has established that the positions of the main lines of both emission and absorption spectra coincide fully with the respective lines of monocrystalline phosphors of the same composition (2). However, in the case of both absorption and emission spectra sublimate-phosphors give an entirely different relation between the intensities of long-wave and short-wave lines than monocrystalline phosphors. Again, besides the ultraviolet and visible lines in the emission spectra of sublimate-phosphors, there appears a third line, in the infra-red zone. There are some means of regulating the intensivity of some of the lines, which may change the colour of luminescence to a certain extent (for KCl + TlCl from bluish-green to orange, including pure white).

Depending on the conditions of heating and the concentration of the activation it was found possible to vary widely the relationship between prolonged and momentary luminescence of sublimate-phosphors (from full absence of prolonged luminescence to quite intensive luminescence lasting for hours). The law of decay fits well into a curve formed by superposing an exponent curve on to a hyperbola of the second order, the relation of these components varying quite explicably with the concentration of the activator.

A study of the relationship between the brightness of the sublimate-phosphors and the concentration of the activator showed that the optimum activator concentration is considerably greater for them than for monocrystallic phosphors of the same composition, and in accordance with this the luminescence of the former is considerably brighter than that of the latter, and often reaches magnitudes comparable with the brightness of technical phosphors.

Another interesting new phenomenon was observed, consisting in the fact that filling the container holding the «alkali-halide salt + activator» layer with oxygen, or with air has the same action as heating, *i. e.* the layer becomes a phosphor without additional thermal treatment.

It was found that alkali-halide sublimate phosphors give good cathode luminescence, the high brightness of which in combination with the excellent structural qualities of screens covered with sublimate-phosphors, make the latter quite eligible for technical use.

Alkali-halide sublimate-phosphors were also found to be X-ray luminescent. But their luminescence in this case is not very bright, which makes this phenomenon interesting only from the standpoint of those possibilities which arise for the study of the nature of this kind of luminescence due to the simplicity of composition and structure of alkali-halide phosphors.

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PHYSICS

EXPERIMENTS WITH ROCK-SALT CRYSTALS

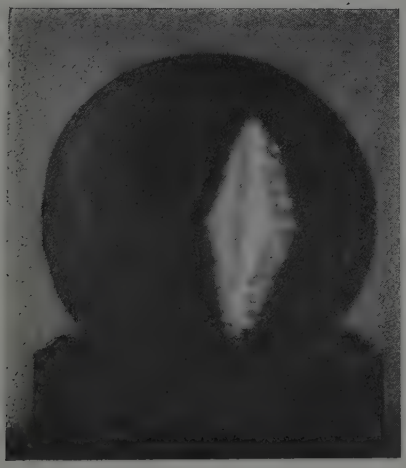
By P. I. LUKIRSKY, Corresponding Member of the Academy

The investigation of the field emission of electrons is usually carried out with sharp conical needles of tungsten or molybdenum. Upon heating *in vacuo* the vertices of the cone become round with a hemisphere at their end. The spatial distribution of the field-emission from such a hemisphere shows that the sphere is monocrystalline, for this distribution has the same symmetry as the crystal of the substance under investigation. The recrystallization and the change in the shape of the cone take place at a temperature much lower than the melting point. The change in the shape of the emitters, *i. e.* the transformation of the vertex of the cone into a hemisphere, is a result of surface tension. It seems that in this case the surface of the monocrystal should have a shape different from a sphere because in a crystal the surface tension varies with the crystallographic direction.

Some experiments were made in order to elucidate this question. The experiments were carried out with large crystals, for the investigation of the shape of very small emitters was too difficult. The monocrystalline spheres were made of rock-salt crystals a few centimeters in diameter. After polishing they were heated in a furnace at a temperature considerably lower than the melting point of the rock-salt. In different experiments the temperature ranged from 720 to 760° C. After heating during several hours some figures were formed on the surface of the sphere, corresponding to the symmetry of the crystal. At the ends of the 1, 0, 0 axes, passing through the centre of the sphere, octahedral figures were formed. At the ends of the 1, 1, 0 axes there appeared rhombic figures. At the ends of the 1, 1, 1 axes pyramids with symmetry of the third order were clearly seen. Fig. 1 presents photographs of the corresponding portions of the sphere surface. The first photograph shows three bright lines diverging from the end of the axis 1, 1, 1. The outer ends of these lines are the ends of the axis 1, 0, 0. On the same photograph three weak lines, bissecting the angles between the bright lines, are seen. On the second photograph the portion of the surface surrounding the 1, 0, 0 axis is given; the third photograph shows the region into the neighbourhood of the end of the 1, 1, 0 axis. The fourth photograph shows the same rhombus as the photograph No. 3. It should be mentioned that the figure that is formed in the vicinity of the 1, 1,1 axis is repeated eight times on the surface of our sphere, and that the ends of the respective 1, 1, 1 axis pass through the centres of these figures. The other figures formed round the other axes are also repeated strictly according to the symmetry of the axis about which the rotation is effected. The slopes on both sides of the bright lines diverging from the 1, 1, 1 axis as a centre, naturally form an octahedral figure around the 1, 0, 0 axis, because four bright lines go to the end of each 1, 0, 0 axis. Two bright lines from one 1, 1, 1 axis form two sides of the rhombus shown on the photographs 3 and 4. One of the diagonals of this rhombus connects the ends of two 1, 0, 0 axes; the other, the shorter one, the ends of two 1, 1, 1 axes. Comparing

1

2



3

4

Fig. 1. 1. (1, 1, 1). 2. (1, 0, 0). 3. (1, 1, 0). 4. (1, 1, 0)

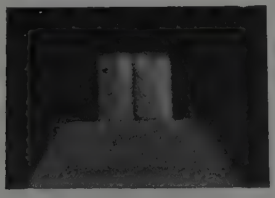


Fig. 2. Cylinder with generatrix parallel to 1, 1, 0 axis

these pictures one can easily see that the monocrystalline sphere of rock-salt is transformed upon heating into a polyhedron with forty eight faces. This transformation may also be proved by the following experiment. If the sphere, after heating is over, is made to roll over a smooth horizontal plane, it will be found to travel with abrupt turns along a zigzag trajectory. Its rolling is, moreover, accompanied by a series of knocking sounds. The obtained figure with forty eight faces does not seem to be a regular geometric hexaoctaedron. In fact, the axis 1, 1, 1 protrudes more than the axis 1, 0, 0. The axis 1, 1, 0 does not practically protrude at all. The planes which form a regular hexaoctaedron possess the indices (3, 2, 1); but the indices in our figure are more complicated. It may be remarked that the experiment can be repeated several times with the same crystal. Only the surface of the crystal has to be polished then so as to give it again the form of a sphere. After heating the same figure will reappear on its surface. The change in length of the different crystallographic axes upon heating is very small. For a sphere two centimeters in diameter the difference is a magnitude of the order of ten microns. This is partly due to the absence of sharp edges or vertices in our figure. All of them are slightly rounded out. To become convinced of that one may take a monocrystalline cylinder instead of a sphere. Fig. 2 is a photograph of such a cylinder. After heating several faces are formed on its surface. When rolled on a horizontal plane, the cylinder always stops on its faces. When the plane is inclined, the cylinder turns over on to the next face. But to produce this result the plane must be inclined more gently than in the case of a sharp edge between the faces. One face passes into another gradually. The determination of the exact form of the figure obtained is rather difficult because the heating of the cylinder somewhat distorts its shape owing to residual deformation.

Let us now consider the nature of all these phenomena. As has been mentioned above, the surface tension in a crystal is variable with the crystallographic direction. Accordingly, in a monocrystalline sphere tangential surface forces must be at work causing the surface particles to move towards regions of high tension. If the temperature of the experiment does not preclude a free movement of particles, their migration toward these regions is bound to take place. The obtained figure must be that corresponding to equilibrium conditions, at which the free energy is known to have a minimum value for a given volume of the crystal. On a monocrystalline sphere all crystallographic directions are equally well defined. If the polyhedron obtained by heating is a closer approximation to an «equilibrium» figure than is a sphere, then the surface tension at its edges and, especially, at its vertices is greater than on its faces. So we arrive at the conclusion that in our case the surface tension has a maximum value in the direction of the 1, 1, 1 axes, because these axes protrude more than others. What is obtained in this way may be either only an approximation to the equilibrium figure or it may be an intermediate equilibrium form. The latter alternative depends upon the existence of many minima of free energy.

No further transformation of our figure was observed in spite of very long heating. However, the problem of wether or not the figure obtained is one of equilibrium cannot be considered as definitely cleared. The formation of smooth edges and vertices, *i. e.* the existence of regions with complicated indices, is probably due to the fact that the surface tension varies but little for different crystallographic directions and has no discontinuities. The derivative of the surface tension may be discontinuous. Let us now consider the mechanism which leads to the change in the form of our sphere.

The formation of an equilibrium figure has its origin in different processes. Under the conditions of our experiment it may result from repeated evaporation and condensation of vapour, or from the migration of the particles on the surface of the crystal. The second possibility seems more probable, since the energy of activation of migration is considerably smaller than the heat of evaporation. Besides, control tests in which the crystals were weighed before and after the experiment, and the investigation of the phenomenon in saturated and non-saturated vapour have shown that the evaporation, if it occurs at all, does not determine the

rate of the process. We must now examine the rôle played by the state of the crystal surface. In fact, the process of polishing the crystal leaves a surface that is covered with scratches and distorted. But the migration of the particles must have a healing effect on the surface because the total surface area of the crystal tends to a minimum. Special experiments have confirmed this assumption.

If the surface of a crystal is purposely made rough, then after heating it becomes smooth and reflects the light. The migrating particles will pass, under the action of tangential forces mentioned above, to places with a greater surface tension. The rate of this process must depend on the temperature of the body. If we consider the process of migration as a phenomenon of surface diffusion, we must ascribe some energy of activation Q to it. But the diffusion proceeds under the action of a force caused by the difference of surface tension in different places of the crystal surface. The number of particles migrating in unit time is proportional to $\frac{d\sigma}{ds} e^{-Q/RT}$, where $d\sigma$ is the change of surface tension along the length ds. This equation is analogous to that which serves to describe current conduction in a crystal, where diffusion takes place under the action of a small force. A detailed investigation of the phenomena observed is in progress.

I wish to express my sincere thanks to M. N. Flerova for the many measurements carried out in order to determine the true shape of the obtained polyhedral figure, and for other help in the course of these experiments.

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PHYSIQUE APPLIQUÉE

SUR UN CAS DÉGÉNÉRÉ DU PROBLÈME GÉNÉRAL DE RÉGULATION DIRECTE

Par A. ANDRONOW et N. BAUTIN

(Présenté par L. I. Mandelstam, de l'Académie, le 31. V. 1944)

Certains systèmes intéressants de régulation directe, en particulier certains systèmes réglant la pression et la température, possèdent les propriétés caractéristiques ci-dessous.

En analysant leur fonctionnement: 1) il est inadmissible de négliger les phénomènes transitoires dans l'organe par l'intermédiaire duquel la grandeur à mesurer agit sur l'indicateur (l'organe de mesure); 2) il est inadmissible de négliger le frottement de glissement (le frottement coulombien) dans ce dernier; mais par contre: 1) on peut négliger l'inertie de l'indicateur et 2) on peut négliger le frottement visqueux dans celui-ci.

Ce cas dégénéré du problème général de régulation directe a été examiné par W. Schmidt ([1], [2]) à l'aide d'une intégration numérique des équations du mouvement. Il sera montré ici que le problème peut être traité analytiquement. L'étude analytique complète et précise les résultats de Schmidt sur un point essentiel: elle permet d'établir les conditions d'existence et les caractéristiques quantitatives des auto-oscillations éventuelles, auto-oscillations qui ne sont pas mentionnées dans le mémoire cité.

1. Les équations du mouvement pour le cas dégénéré qui nous intéresse s'écrivent, compte tenu des simplifications usuelles, sous la forme *

$$-a\xi+b\eta+Q=0 \quad \left\{ \begin{array}{l} Q=K \text{ pour } \frac{d\xi}{dt}<0;\ Q=-K \text{ pour } \frac{d\xi}{dt}>0; \\ -K\leqslant Q\leqslant K \text{ pour } \frac{d\xi}{dt}=0 \end{array} \right\} \qquad (1)$$

$$\frac{d\eta}{dt}=\sigma(\zeta-\eta);\ \frac{d\zeta}{dt}=-\frac{a}{b}\frac{1}{T}\xi$$

ξ, η, ζ étant les écarts entre les positions actuelles et les positions d'équilibre de l'indicateur, de l'organe intermédiaire et du dispositif, et $a>0$, $b>0$ des constantes, caractérisant la force agissant sur l'indicateur.

$K>0$ est le frottement de glissement dans l'indicateur, $\sigma>0$ une constante caractérisant la rapidité du phénomène transitoire dans l'organe intermédiaire, $T>0$ la constante de temps du dispositif.

Ecrivons

$$\frac{a\xi}{2K}=x;\ \frac{b\eta}{2K}=y;\ \frac{b}{2K}(\zeta-\eta)=z;\ \sigma t=t';\ \frac{1}{T\sigma}=\alpha\ (\alpha>0)$$

---

* W. Schmidt ([2]), p. 100. On passe aux notations de Schmidt en écrivant $\xi=s-s_{II}$; $\eta=z_R-z_{II}$; $\zeta=z_A-z_{II}$; $a=\frac{P_{max}}{s_{max}-s_{min}}$; $b=\frac{P_{max}}{z_{max}-z_{min}}$; $Q=R_R$

et considérons x, y, z comme des coordonnées cartésiennes. Le système (1) prend l'aspect

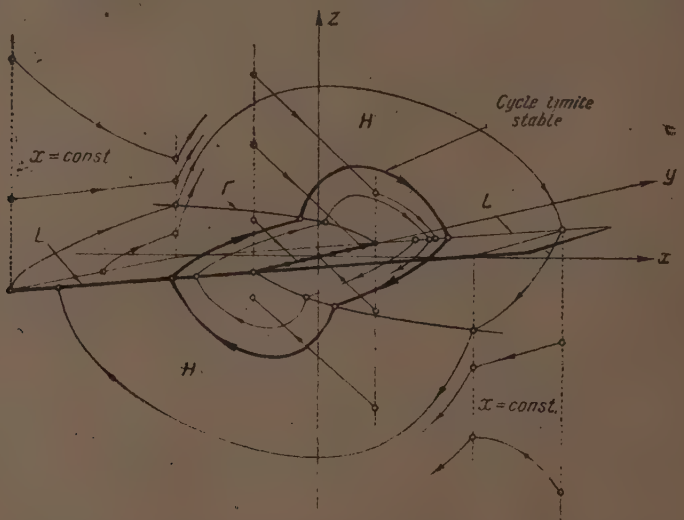
$$\frac{dx}{dt'} = f(x, y, z); \quad \frac{dy}{dt'} = z; \quad \frac{dz}{dt'} = -\alpha x - z \tag{2}$$

où $f \equiv 0$ entre les plans $x - y = +\frac{1}{2}$ et $f = z$ dans les demi-plans

$$(H): \quad x - y = \frac{1}{2}, \; x < 0 \text{ et } (H'): \quad x - y = -\frac{1}{2}, \; z > 0$$

Nous examinerons les solutions du système (2) déterminées par la condition de continuité de $x(t')$, $y(t')$, $z(t')$ aux points de discontinuité de $f(x, y, z)$.

2. En vertu de (2): 1) l'extension en phase à 3 dimensions est remplie de morceaux de trajectoires situés dans les plans parallèles $x = \text{const}$; 2) la divi-



sion en trajectoires des demi-plans H et H' bornant cette extension en phase comprend soit des morceaux de trajectoires allant à un noeud stable (si $4\alpha - 1 < 0$), soit des morceaux de spirales (si $4\alpha - 1 > 0$); 3) le segment $x = z = 0$, $|y| \leqslant \frac{1}{2}$ est un segment de repos. Le point figuratif se mouvant dans les demi-plans H ou H' ou bien arrive directement à l'extrémité du segment de repos, ou bien arrive sur les demi-droites (L): $x - y - \frac{1}{2} = 0$, $z = 0$, $x < 0$, ou (L'): $x - y + \frac{1}{2} = 0$, $z = 0$, $x > 0$, d'où il part de nouveau dans l'espace, passant d'un demi-plan à l'autre.

Appelons transformation S^+ (ou S^-) le passage d'un point de la demi-droite L (L') sur le demi-plan H' (H), et transformation E^+ (E^-) le passage d'un point du demi-plan H' (H) sur la demi-droite L' (L).

La transformation $T^+ = S^+E^-$ transforme les points de la demi-droite L en points de la demi-droite L', et la transformation $T = S^+E^+S^-E^-$ transforme L en elle-même.

Le problème considéré à trois dimensions est donc une transformation ponctuelle d'une droite en elle-même.

3. La transformation S^+ transforme la demi-droite L en une courbe Γ située dans le demi-plan H':

$$x = \frac{1}{\alpha(1 - \tau - e^{-\tau})}, \quad z = -\frac{1 - e^{-\tau}}{e^{-\tau} + \tau - 1} \quad (0 < \tau < \infty) \tag{1'}$$

Trouvons dans le demi-plan H' le lieu géométrique des points tels que la transformation E^- ne change pas la valeur absolue de leur distance au plan $x=0$. On montre facilement que tous ces points se trouvent sur la demi-droite $z=kx$, k étant déterminé par l'équation

$$\alpha e^{\frac{2}{\sqrt{4\alpha-1}}\operatorname{arctg}\frac{k\sqrt{4\alpha-1}}{k+2\alpha}} = k^2+k+\alpha \quad (0<\operatorname{arctg}<\pi) \tag{3}$$

Les points du demi-plan H' sont divisés par la droite $z=kx$ en trois classes: a) ceux appartenant à la demi-droite $z=kx$; la transformation E^- ne change pas leur distance au plan $x=0$; b) ceux pour lesquels $z>kx$; la transformation E^+ les rapproche du plan $x=0$: c) ceux pour lesquels $z<kx$; la transformation E^+ les éloigne du plan $x=0$.

Si $z=kx$ ne coupe pas la courbe Γ (si $k<-\alpha$), la transformation $T^+=S^{-1}E^-$ rapproche les points de la courbe Γ du plan $x=0$. Le segment de repos est alors stable. Si $z=kx$ coupe la courbe Γ (si $k>-\alpha$), tout point de L suffisamment proche du segment de repos s'éloigne de celui-ci. Le segment de repos est alors instable. Si $k=-\alpha$, la demi-droite $z=kx$ est tangente à la courbe Γ à l'origine des coordonnées. Faisant dans (3) $k=-\alpha$, nous trouvons la valeur $\alpha=\alpha_0=3.04$ pour laquelle le segment de repos change la stabilité.

4. Supposons que $z=kx$ coupe la courbe Γ. Il résulte de la définition de k que l'intersection P (elle est unique) est invariante par rapport à la transformation $T'=E^+S^-E^-S^+$. La transformation T' transforme tout point de l'arc de courbe Γ en un point appartenant également à Γ et plus rapproché de P. La transformation T' étant itérée, la suite des points de Γ converge vers P. La transformation T' transforme tout point du demi-plan H' n'appartenant pas à Γ en un point de la courbe Γ. Le point P est donc un point invariant stable. Le mouvement périodique stable qui lui correspond se compose de morceaux de trajectoires de phase situés dans les demi-plans H et H' et de morceaux de trajectoires compris entre ces demi-plans.

5. La période $\tau^*=2(\tau_0+\tau_1)$, où τ_0 et τ_1 sont les durées de parcours sur les morceaux de trajectoires appartenant au mouvement périodique compris respectivement entre et dans les demi-plans H et H', peut s'écrire sous la forme

$$\tau^*=2\ln\left\{\frac{k^2+k+\alpha}{k+\alpha}\right\}$$

où k est déterminé par la formule (3). τ^* augmente indéfiniment lorsque le mouvement périodique se contracte vers le segment de repos.

6. Ainsi qu'il a été montré, le phénomène de régulation converge, quelles que soient les conditions initiales, vers l'état d'équilibre, si $\alpha<3.04$. Si $\alpha>3.04$, le dispositif de régulation est le siège d'auto-oscillations dont les caractéristiques quantitatives peuvent se calculer facilement. Dans le système considéré le frottement de glissement (le frottement coulombien) est la cause d'instabilité et d'auto-oscillations, car lorsque $Q\equiv 0$ l'état d'équilibre est stable, et il n'y pas d'auto-oscillations quelle que soit la valeur de α*.

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* Ces conclusions résultent de l'idéalisation adoptée. Si l'on admet que la masse de l'indicateur $m\neq 0$, l'état d'équilibre est instable lorsque $Q\equiv 0$ quels que soient α et m.

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CHEMISTRY

A NEW VOLUMETRIC (VANADATOMETRIC) METHOD OF DETERMINING OSMIUM

By V. S. SYROKOMSKY

(Communicated by I. I. Chernjaiev, Member of the Academy, 12. V. 1944)

The only volumetric method of determining osmium known up till now has been the classical indicator method. An iodometric method was proposed for this metal by Klobbie (1), and somewhat improved and changed by Krauss and Wilkin (2), and again, by Crowell and Kirschman (3). This method, however, is not very satisfactory due to the great difficulty in observing the equivalent point and to the necessity of titrating in a current of invert gas, and for these reasons it is not used in practice. Besides this, Crowell and his collaborators proposed a number of potentiometric methods of determining osmium (4), which consisted mainly of reducing the osmium compounds to trivalent ones with titanious and chromous salts. These methods, especially those involving titration with bivalent chromium salts, give very accurate results, but are also unsatisfactory for serial determinations due to inconveniences in storing the titrated solutions and in titrating in an atmosphere of a neutral gas (N_2, H_2). Besides, this method has all the faults peculiar to any potentiometric method of observing the equivalent point.

The disadvantages mentioned made us enter into a search for more convenient methods of determining osmium, which would be sufficiently accurate and simple to be applied in serial determinations. It was considered, moreover, desirable to make use of some redoxy method in which the equivalent point could be pronouncedly fixed with the help of new redoxy indicators, since complex ions of osmium colour their solutions strongly. We tested permanganate, bichromate and vanadate as oxidizers, and found that only the last mentioned offered a possibility of developing a speedy and accurate volumetric method of determining osmium.

Experimental. For this work an alkali solution of osmium tetroxide was prepared, and its titre determined after the usual gravimetric method, by precipitating osmium as the sulphide and then calcining the precipitate in a current of hydrogen. Four coinciding determinations showed the titre of the osmium solution to be 48×10^{-5}. We considered the most convenient method of reducing osmium solutions to be with metallic bismuth. This metal which possesses a relatively high normal potential of $+0.32$ V, has a number of advantages over other reducing agents: a) bismuth ions pass into solution only in stoicheiometric quantities according to the equation:

$$3Os^{+8} + 4Bi \rightarrow 3Os^{+4} + 4Bi^{+3} \qquad (1)$$

due to the insolubility of bismuth in weak acids.

b) Bismuth is quite pure and does not contain admixtures (Fe, Pb, Sb, *etc.*) in quantities large enough to affect the results. The osmium solutions, up to 4—6 *N* were acidified with sulphuric acid and reduced by passing them through a bismuth reducer of the type first proposed by Alimarin (5) for reducing ferric salts. After

reducing, an excess of 0.01 *N* ammonium vanadate solution was added, and the excess was immediately titrated with a 0.01 *N* solution of Mohr's salt in the presence of a 0.2 per cent solution of phenylanthranylic acid as the indicator to a change in colour from cherry-red to yellow-orange. The transition is quite pronounced and easily noticed for one drop of 0.01 *N* ferrous solution.

Direct titration of reduced osmium solutions with vanadate does not give reproducible results, since the indicator becomes oxidized before the equivalent point is reached, which results in a blurred transition. Typical results of vanadatometric osmium determinations are given in the following table.

Taken Os, g	Expended 0.01 *N* V^{+5} solution, ml	Detected Os (taking the equiv. wt. as 95.75), g	Taken me Os (at. wt. 191.5)	Expended me V^{+5}
0.0024	2.45	0.00237	0.01254	0.02517
0.0048	5.00	0.00479	0.02508	0.05014
0.0072	7.50	0.0072	0 03762	0.07521
0.0096	10.00	0.0096	0.05016	0.1028

Discussion of Results. In order to oxidize one milliequivalent of Os it is necessary to expend exactly two me of vanadium; this shows that osmium is oxidized two valencies, probably according to the following equation:

$$Os^{+4} + 2V^{+5} \rightarrow Os^{+8} + 2V^{+4} \qquad (2)$$

The fact that during oxidation with vanadate there is no odour of OsO_4, as in the case of permanganate and bichromate, also goes to prove that vanadate oxidized osmium only to the hexavalent state. $KMnO_4$ oxidizes the reduced solution to colourless octivalent compounds, but the results are inaccurate owing to part of the OsO_4 being lost with the current of CO_2. Vanadate in acid solution is a very convenient oxidizing agent, since the redoxy potential system V^{+5}/V^{+4} can be varied within wide limits, from 0.95 to 1.45 V (6) depending on the concentration of sulphuric acid.

After fixing the acidity of the vanadate solution and the osmium test-solution at somewhere between 4 and 8 *N* in relation to sulphuric acid, such a potential (about 1.08—1.12 V) is created that will oxidize Os^{+4} to Os^{+6}, but lies considerably below the potential necessary to oxidize to Os^{+8} (probably 1.2—1.25 V). The reaction between vanadium and the indicator being quite sensitive, and the indicator error being insignificant (7), high accuracy is guaranteed in determining osmium within the range of concentrations studied, which can probably be enlarged considerably.

Procedure for Determining Osmium. A bismuth reducer can be made out of an ordinary 50 ml burette with a glass faucet. A thin layer of glass wool is put into the narrow part of the burette (above the faucet), and on top of this, a layer of about 100 mm of powdered bismuth. The bismuth is ground in a mortar, and the powder is sifted to select the grains having diameters from 0.3 to 0.6 mm. These grains are used in the reducer. The reducer is washed two or three times with 4 *N* sulphuric acid, having a 2—3 mm layer of acid above the bismuth layer each time, and then all is ready to begin reducing.

The osmium solution is acidified with H_2SO_4 so that its acidity lie between 4 and 6 *N*, and is quickly transferred to the reducer, washing two or three times with a few ml of 6 *N* H_2SO_4. The volume of the reduced solution together with the wash should not exceed the capacity of the reducer (about 40 ml). The velocity of the solution running through the reducer should be regulated by opening or closing the faucet to within 4—8 ml per min.; the osmium solution is allowed to run out until its level is 2—3 mm above the bismuth layer, and then the reducer is washed

three times with 6 N H_2SO_4, using 15—20 ml each time and without exposing the bismuth layer. If the reducer has been charged correctly, the operation of reduction should not take more than 20—25 min. The reduced solution is collected in an Erlenmeyer flask 250 ml in capacity, an excess of 0.01 N ammonium vanadate solution in 6 N H_2SO_4 and 3—4 drops of 0.2 per cent indicator solution (0.2 g phenylanthranylic acid is heated with 100 ml of the 0.2 per cent solution) are added, and then the excess vanadate is titrated with a 0.01 N solution of Mohr's salt in 6 N H_2SO_4. The correlation between the Mohr's salt and vanadate solutions is found, and then the number of ml of 0.01 N vanadate solution expended in oxidizing osmium is calculated. The titre of the ammonium vanadate solution is determined by finding the active V_2O_5 content. For this purpose a few weighed portions of about 0.2—0.3 g each of chemically pure NH_4VO_3 are carefully calcined in a platinum crucible at 500—600° C to constant weight, the V_2O_5 residue being wetted several times with one drop of HNO_3 of 1.4 sp. gr. An alternate method of finding the titre of the solution is the volumetric method with a weighed portion of Mohr's salt, in which the ferrous content has been determined by titrating with permanganate, or, better, thrice recrystallized bichromate in the presence of phenylanthranylic acid.

Calculation: weight of Os in gs $= 0.09575\ rk$ where r is the number of ml of vanadate expended in titrating; k is a coefficient for reducing the solution exactly to 1 N; and $0.09575 = \frac{191.5}{2 \cdot 1000}$ is the milliequivalent weight of osmium, calculated from equation (2) mentioned above.

The experimental part of this work was done by N. N. Proshenkova.

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PHYSICAL CHEMISTRY

THE SORPTION AND THE HEATS OF SORPTION OF VAPOURS AND THE STRUCTURE OF ACTIVATED CHARCOALS

By A. V. KISSELEV, V. P. DREVING and A. D. RUNOV

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It has been shown by one of us in collaboration with K. D. Shcherbakova that during the adsorption of surface-active substances from aqueous solutions by activated charcoals the micropores of the latter, which have a high adsorption potential with respect to these organic substances, become tightly packed with their molecules forced out of the polar aqueous phase (1). In that work it was found that the maximum adsorbed volume of the fatty acids and alcohols containing more than three carbon atoms per molecule is practically independent of the length of the hydrocarbon radical, and is a measure of the volume of the micropores of the charcoal. In the present paper we shall test the validity of these conclusions against the results of a study of the isotherms and sorption heats of the methyl alcohol vapour on the same specimens of activated charcoals.

The measurements were made with a set-up similar to the one described elsewhere by Dubinin and Zaverina (2), modified to enable simultaneous measurement of the heats of adsorption by including another adsorption tube in which a weighed sample of the adsorbent was placed, parallel to the one containing the McBain quartz balance. First both tubes were enclosed in an oven and evacuated at a temperature of 420° C to a pressure of less than 10^{-5} mm. Then the oven was removed and replaced by an electrical calorimeter; into its inside compartment was placed the tube with the large weighed sample of the adsorbent, and the tube with the McBain balance was put into the petroleum jacket of the calorimeter. The temperature in the jacket was controlled by a photo-relay. Inside the calorimeter there was a resistance thermometer with a sensitivity of 0.0001° C, which made it possible to register the extremely small heat effects accompanying each slight introduction of vapour. The heat capacity of the system was measured with the aid of an electric heater (3). This combination of a McBain quartz balance with a calorimeter set-up proved a convenient method of obtaining points on the isotherm and the corresponding heats in one and the same experiment.

In Fig. 1 are given some of the isotherms obtained. All of them have one feature in common: a point of inflection at a relative pressure of about 0.53, beyond which a sorptional hysteresis loop begins. The latter refers to capillary condensation in the larger pores of the adsorbent (4). In this region the heat of sorption was found to be close to the normal heat of condensation, which confirms the presence of capillary condensation (4).

At relative pressures less than 0.53, sorption is due to the adsorptional field of the charcoal. The differential heat of adsorption in this region considerably exceeds the heat of condensation. The molecules of the sorbate accumulate gradu-

ally in the adsorption field, and fill it completely before capillary condensation starts. Therefore we can determine the volume of the pores filled during the adsorption process by multiplying the ordinate of the starting point of the hysteresis loop by the molar volume of the liquid alcohol, disregarding its possible compression.

In Table 1 volumes calculated in this manner are compared with the maximum volumes of the surface-active substances adsorbed from aqueous solutions that were obtained previously [1]. The values are in close agreement. Thus, the volume of the micropores of activated charcoals can be determined: 1) by measuring the constant maximum volume of fatty acids or alcohols adsorbed from aqueous solutions [1], and 2) by measuring the volume of the methyl alcohol vapour condensed under the influence of the adsorption field before capillary condensation starts.

Table 1

Volumes of the Micropores of Activated Charcoals in cm^3/g

Method	Charcoal samples							
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Adsorption of fatty acids and alcohols from aqueous solutions	0.28	0.27	0.38	0.26	0.31	0.33	0.31	0.52
Adsorption of vapour of methyl alcohol at the beginning of capillary condensation	0.28	0.26	0.39	0.24	0.31	0.35	0.30	0.52

The separate stages of the vapour sorption process corresponding to the filling up of the micropores due to the adsorption forces and to the subsequent filling up of the bigger pores during capillary condensation, become clearer if the heats of sorption of the vapour are considered. Part of the results we obtained are given in Fig. 2.

The curve of the differential heats of sorption falls into three parts: 1) a region of high heats, about 18000—20000 calories per mole, and for some specimens even up to 25000—30000, which fall off rapidly in conformance with the abrupt decrease in the slope of the initial part of the adsorption isotherm; 2) a region of nearly constant heats, about 14000—120000 calories per mole, exceeding the heat of condensation by only 50—30 per cent, which conforms to that part of the isotherm corresponding to a relative pressure from 0.1 to 0.53, *i. e.* to the start of capillary condensation, and, finally, 3) a region where the heats decline rapidly to the normal heat of condensation, corresponding to the sorption hysteresis loop.

The broad middle region of approximately constant differential heats of adsorption of the methyl alcohol vapour was reproduced with great accuracy for all the charcoals studied. It corresponds to the filling up of the micropores by the bulk of the adsorbate. At the transition to average, nearly constant, heats probably the filling up of especially active spaces and the covering of the rest of the charcoal surface by a first layer is completed, and the formation of subsequent layers begins, right up to complete filling up of the volume of the micropores, which precedes the start of capillary condensation. However, these stages of adsorption overlap somewhat, owing to the fine structure of the walls of the micropores, detracting from the clarity of the general picture.

Since the adsorption potential of the charcoal, as a non-polar adsorbent, slowly decreases with the distance from the surface, and since it is locally intensified in the finest cracks, it is hardly possible in general to determine from the adsorption isotherms the transition from monomolecular to polymolecular layer. However, as a first approximation it may be assumed that the transition from the initial,

high molar heats of adsorption to medium, approximately constant values corresponds to the filling up of all the most active cracks in the surface of the micropores.

The fact that the molar heat remains constant as adsorption of the bulk of the vapour continues, gradually filling up in the form of liquid the entire

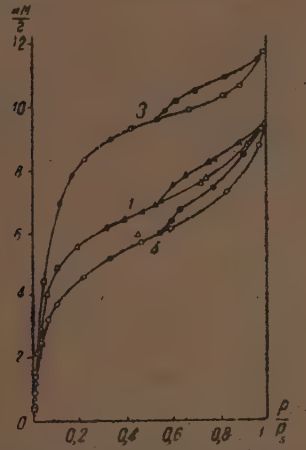

Fig. 1. Sorption and desorption isotherms of methyl alcohol vapour for certain specimens of activated charcoals

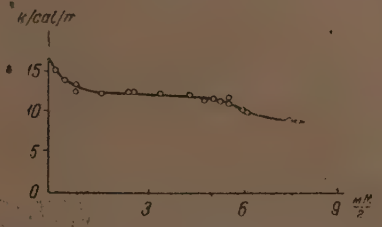

Fig. 2. The dependence of the differential heat of sorption by charcoal of methyl alcohol vapour upon the quantity adsorbed

volume of the micropores, may be explained as follows: the fall in potential of the charcoal with an increase in distance from the walls is compensated by the increase in potential of the film of the previously condensed liquid with a decrease of the free volume in the central part of the micropore.

The region of nearly constant heats of adsorption may be explained also by the primary covering of the uniform, less active areas of the surface of the micropores, after the active areas have been filled up. In order to settle this problem it is necessary to estimate the effective cross-sections of the micropores and the areas of the specific surface. At present, however, we are not yet in the possession of reliable independent methods of determining these magnitudes for charcoals.

Simultaneous study of the differential heats of adsorption and the adsorption isotherms enables us to establish in outline the distribution of the adsorption potential in charcoal pores. In the first place, it will be possible to indicate the point where the adsorption space is filled, according to the sharp decrease in the heat of adsorption from 12 000 calories per mole to the normal heat of condensation. This gives a third independent method of determining the volume of the micropores. Secondly, investigations of the heats of adsorption at lower pressures indicate the distribution of the adsorption potential within the micropores of the charcoals. Adsorption of the initial quantities of vapour, which fill up in the condensed state only about 10—20 per cent of the volume of the micropores, is characterized by quite large differential heats of adsorption. Adsorption of the vapour filling up the remaining 80—90 per cent of the volume of the micropores takes place at practically constant heats of adsorption, which is less than one and-half times the heat of condensation.

In this connexion the evolution of the heat of wetting, which is an integral effect, is due only to that part of the wetting liquid which gets into the adsorption space of the charcoal pores, *i. e.* into its micropores. The liquid which fills the bigger pores will for all practical purposes not figure in the evolution of the heat of wetting. On the other hand, the most active part of the volume of the micropores will account for only a comparatively small fraction of the heat of wetting, since from Fig. 2 it is seen that the main part of the area under the curve of the

differential heats of adsorption, representing the integral effect, lies in the mid region. Therefore the heat of wetting should be roughly proportional to the volume of the micropores of the charcoals; the nature and fine structure of the surface of the micropores and the ratio of the volumes of the active areas to the total volume of the micropores give rise to deviations from this rule, which are different for different kinds of charcoal. In Table 2 are given results of measurements of the heat of wetting by methyl alcohol of several of the specimens studied, and also the ratios of these quantities to the volumes of the micropores; the latter are practically constant. Therefore the volume of the micropores of activated charcoal may be roughly estimated by dividing by 60 its heat of wetting by methyl alcohol expressed in calories per gram (a fourth, approximate method).

Table 2

Heat of Wetting of Charcoals by Methyl Alcohol

Charcoal sample	No. 1	No. 2	No. 3	No. 4	No. 5
Calories per gram	18.7	15.8	22.3	13.8	19.8
Volume of micropores (in cm^3/g)	0.28	0.26	0.38	0.25	0.31
Calories per cm^3 of the volume of micropores	67	71	59	55	64

We note, finally, that the sharp transition to sorptional hysteresis connected with the fall in the heat of sorption to the heat of condensation, makes it possible to separate a second group of bigger pores which are filled up in the process of the capillary condensation of the vapour. For all charcoals this process begins at the same effective radius, namely approximately 12 Å. The volumes of these «transitional» pores fluctuate for different specimens from 0.02 to 0.17 cm^3/g, and are distributed differently with respect to their effective radii.

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GEOLOGY

ON THE SUBDIVISION OF UPPER CARBONIFEROUS

By V. E. RUZHENCEV

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For many years it was the common practice to apply to the Upper Carboniferous of the Urals the term of Uralian. It has recently been proved, however, that this term was meant to cover the whole thickness of carbonate rocks from the *Triticites* beds to the so-called Sarga and Krasnoufimsk limestones inclusive of the Artinskian age.

Therefore some authors, as for instance Stepanov ([6]), suggested to subdivide the Upper Carboniferous into two stages, the Gzhelian and the Uralian. To the former are referred the *Triticites* beds; and to the latter, the beds with *Schwagerina*, *Pseudofusulina moelleri* Schellw. and *P. urdalensis* Raus. As to the beds with *Parafusulina lutugini* Schellw., in some cases they belong to the Uralian, and in other cases, to the Lower Permian.

The present author does not find it advisable to apply the name of Uralian stage to a definite portion of Upper Carboniferous deposits, so much the more to a definite part of the Permian, since the term of «Uralian» wasin troduced by Lapparent ([10]) to designate the upper division of the Carboniferous system. The term «the Uralian stage» should therefore be excluded from the stratigraphic nomenclature.

In accordance with the boundary between the Carboniferous and the Permian systems as actually adopted by most investigators, to the Uralian division are referrable the beds lying on the Middle Carboniferous and overlain by the Sakmarian stage of the Permian system, in other words, the *Triticites* beds in the wide sense of the word. It is for this complex of sediments that Stepanov suggests the name of the Gzhelian stage. Now let us consider whether it is rational to introduce this term as a standard one for the whole thickness of the Upper Carboniferous sediments.

It is a familiar fact that the Gzhelian stage was separated out by Nikitin ([2]) on the basis of a study of the sections of the Gzhel River and Rusavkina village. In the conception of this writer the Gzhelian beds were to correspond to the whole of the Upper Carboniferous of the Urals.

This made Tschernyshew ([1]) in his well-known monograph observe that the name «Gzhelian stage» adopted in the above extent is superfluous, corresponding to a more comprehensible name the «Upper Carboniferous division». In Tschernyshew's opinion, the Gzhelian complex of fauna corresponds only to the complex of the Cora horizon. Therefore if the Gzhelian stage be considered in the light of the fauna of topotypical sections, this name «must give place in the literature to the earlier name of Cora horizon». From Tschernyshew's comments quoted above it may be seen that even by the time it was founded the Gzhelian stage was the object of controversy, which in turn led to incorrect correlations. Later, after the *Tegulifera* beds had been separated within the Moscow section, the Gzhelian beds were found to be correlative with the upper part of Upper Carboniferous deposits only. No precise correlation between the Gzhelian stage and the Uralian section can yet be made, however.

Hence we are lacking any ground to adopt the Gzhelian stage as a standard name for the Upper Carboniferous in a strict sense of the word. If the boundary between the Carboniferous and the Permian be drawn at the base of the *Schwagerina* horizon, which is the only correct course, then the «Gzhelian stage» will correspond again to the whole of the Upper Carboniferous, *i. e.* it will become a synonym of the Uralian division. The term «Gzhelian stage» is inadequate also because it is possible now to speak of the subdivision of the corresponding beds, *i. e.* of the Upper Carboniferous in the strict sense of the word, into two stages, of which the lower may be named the Jigulian, and the upper, the Orenburgian.

Jigulian Stage. The corresponding beds, well developed in the lower part of the Jigulian section at the Samara Bend and opened up by the holes drilled there, have already been separated out under the name of the Samara horizon*, which had been previously correlated with the *Teguliferina* beds and referred to the upper part of the Middle Carboniferous. Semikhatova [5] showed that the fauna of the so-called «Samarian» *Choristites* had existed in the Upper Carboniferous time. The presence in the Samara and *Teguliferina* beds of abundant *Triticites* is good evidence that these deposits should be referred to the Upper Carboniferous.

At the Samara Bend and in the Oka-Tsna region three horizons of the scheme of Rauser-Chernoussova [3, 4] should be assigned to the Jigulian stage: C_3^{1-a} with *Triticites montiparus* Möll.; C_3^{1-b} with *T. arcticus* Schellw. and *T. schwagerini-formis* Raus.; C_3^{1-c} with *T. stuckenbergi* Raus., the total thickness of the deposits, primarily limestones, being from 120 to 150 m.

In the Chkalov region to these corresponds a very thick series (about 800 m) of terrigenous deposits of Abzanovo and Zianchurino horizons which contain, particularly the upper one, a rich fauna of *Triticites* of the same composition. The brachiopods occurring in Zianchurino beds resemble those of the *Teguliferina* horizon of the Moscow basin. Among those collected by the authors, the following forms have been determined by Stepanov (the most typical forms only are listed here): *Dictyoclostus praeuralensis* Step., *D. grünewaldti* Krot. var. *bathycolpos* Schellw., *Echinoconchus neopunctatus* Lich., *Thomasina pseudoartiensis* Stuck., *Choristites pavlovi* Stuck., *Ch. norini* Chao var. *russiensis* I. et I., *Brachythyris sokolovi* Tschern. var. *laevis* Lich. Many forms characteristic of the Upper Carboniferous (Auernig beds) of the Carnic Alps are encountered here: *Marginifera pusillus* Schellw., *Avonia curvirostris* Schellw., *Chonetes latesinuatus* Schellw., *Spiriferella zitteli* Schellw.

Particular attention should be given to small fauna of ammonites, found by the author also in the Zianchurino horizon. The complex of this fauna markedly differs from the well-studied Orenburgian complex in that it contains older forms. Among these, representatives of the genus *Metapronorites* have been encountered with a lanceolate dorsal lobe, resembling in this respect the Namurian and Middle Carboniferous *Pronoritidae*, but in general more highly organized. The genus *Neopronorites*, widely developed in the Orenburgian, has a dorsal lobe with two notches at the end. This points to a phylogenetic leap in the development of the family *Pronoritidae*, at the transition from the Zianchurino horizon to the Orenburgian stage. Quite illustrative is the presence in this complex of representatives of the genus *Parashumardites* which has been found also in the *Teguliferina* beds of Moscow. In North America it is well known only from the Canyon beds, *i. e.* from the lower stage of the Upper Carboniferous. This genus is absent in the rich collection of ammonites from the Orenburgian; instead of it the genus *Shumardites* is widely developed. Characteristic is also the presence in the Zianchurino

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* The stage could also be named the Tzarevokurgan or Samara stage; however, it seems to the present author that these names are not very appropriate. The Tzarevokurgan horizon, separated out by Arkhangelsky [1], comprises only a part of the Jigulian stage—a series of limestones about 15 m thick, exposed at the surface. Moreover, this name would be too long for a stage. The Samara horizon has been separated out by Fredericks [7] as the uppermost member of the Middle Carboniferous. The same term (Samara series) has been used by Grabau [9] to designate beds corresponding to the Kazan stage. Besides, this name is inconvenient because it sounds too much like the Sakmara stage of the Permian system.

fauna of *Marathonites* from the group of *M. parkeri* (Heilp.), which in the USA is known only from the Canyon beds. A detailed study of the fauna will probably permit to establish also other features to distinguish the Zianchurino complex of ammonites from the Orenburgian.

Thus, according to two groups of animals most important for biostratigraphy—ammonites and fusulinids, three horizons of the stratigraphical scheme of Rauser-Chernoussova, on the one hand, and the Abzanovo-Zianchurino beds, on the other, may be proposed as a separate Jigulian stage. The author does not doubt that a further study of the above-named and other groups of fossil organisms will furnish still more ground for such a separation.

Orenburgian Stage. Remarkable sections of deposits of this stage in the terrigenous facies can be seen along the Ural River, west of the Nikolskaia village and north-west of the Ilyinskaia village as well as in certain exposures on the Sakmara River. These beds had previously been separated out as the Orenburgian horizon. Their total thickness is about 500 m. The Orenburgian sections have recently acquired a world-wide renown because of an unexpected discovery of a rich and highly characteristic fauna of ammonites with such typical Upper Carboniferous representatives, as the genera *Uddenites*, *Vidrioceras*, *Shumardites*, *Marathonites*, *Emilites*, *Schistoceras*, *Glaphyrites*, *Aristoceras*, *Neodimorphoceras*, *etc.* A similar fauna had before been known only from the Upper Carboniferous of the USA. Among the fusulinids of the Orenburgian stage is noteworthy the appearance of *Triticites* of the *Triticites jigulensis* Raus., *T. beedei* D. et C., *T. plummeri* D. et C. groups and of *Pseudofusulina*.

At the Samara Bend and in the Oka-Tsna region to the Orenburgian stage should be referred, first, the C_3^{1-d} horizon with *Triticites jigulensis* Raus., and, secondly, the so-called *Pseudofusulina* horizon (C_3^{II}) with a total thickness of the deposits, chiefly dolomites, from 65 to 85 m. For the C_3^{1-d} horizon there are everywhere recorded, in addition to *T. jigulensis* Raus., also *Triticites* from the *T. beedei* D. et C. and *T. plummeri* D. et C. groups, *i. e.* forms which are the most typical for the Orenburgian beds of the Urals as well. The same forms occur also in the *Pseudofusulina* horizon, which makes it similar to the underlying beds.

The ammonites and fusulinids of the Orenburgian stage form peculiar complexes which can readily be differentiated from the corresponding complexes of the Jigulian stage. In the Orenburgian time there developed a peculiar fauna of ammonites, represented by numerous genera. According to data by Rauser-Chernoussova, the study of fusulinids has shown that clear boundaries of the beds are established not only at the base of the Upper Carboniferous, with the appearance of the genera *Triticites* and *Quasifusulina*, but also at the base of the upper portion of the *Triticites* beds, when there appear species of the group *Triticites beedei* D. et C. and *T. plummeri* D. et C. Finally, by suggesting to subdivide the Uralian division of the Carboniferous system into two stages, the author keeps in mind that in the USA the corresponding beds are also subdivided into two stages—Canyon and Cisco (or Missouri and Virgil). It can hardly be any doubt that the subdivision of the Upper Carboniferous deposits here proposed will contribute to a further more detailed study of the separate sections, which in turn will make it possible to work out more detailed correlation schemes.

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MINERALOGY

NATIVE MAGNETIC GOLD

By V. A. OBRUCHEV, Member of the Academy, and D. P. GRIGORIEV

Native gold could hardly be expected to possess magnetic properties.

Magnetic properties have, as it seems, occasionally been recorded for gold by earlier investigators and related by them to the presence in the specimens of paragenetic magnetic minerals, magnetite or limonite; this is why they were neglected and subjected to no study. Plaksin (1) was the first to pay greater attention to this property of native gold when studying this mineral from placers of the Central mine of Mariinsk taiga. Though of usual external appearance, when subjected to spectrum quantitative analysis the magnetic gold from this deposit showed the presence of from 0.1 to 2.0 per cent Fe, along with an Ag content from 2.1 to 9.5 per cent, and Cu from traces to 0.25 per cent. However, when the magnetic gold particles where treated with 0.05 *N* HCl or 0.10 *N* KCN solutions, their iron content would drop sharply to a total loss of Fe; this made Plaksin arrive at a conclusion that the iron in the gold particles studied was related to the surface layer of the mineral only, being no constituent of the gold. For this reason, the magnetic properties of the gold should not be considered as being inherent in the ground mass of the native gold studied by Plaksin.

In 1942 a sample of gold showing peculiar magnetic properties was handed over to V. T. Andrianov, Chief Geologist to the Trust «Yakutzoloto», by one of the mines of this Trust. Part of the gold was sent over to V. A. Obruchev, Member of the Academy. This paper contains the results of the investigation of this gold sample, carried out by D. P. Grigoriev and his co-workers.

The magnetic gold studied has the shape of rounded lamellae, the size of which ranges from fractions of a millimeter to 3 mm, the thickness being tenths fractions of a millimeter, with uneven edges. The shape is no natural one, but must undoubtedly be due to crushing. The surface of the gold lamellae is dull, but in the fracture or in thin-sections they show a metallic lustre and a golden colour distinctive of this mineral.

Each gold particle shows a well-pronounced polar magnetism: it affects the magnetic needle, its different parts attracting or repulsing the northern or southern end of the latter. The gold particles adhere to the magnet; small particles are attracted by larger ones. When a particle is cut, its parts are found also to be strongly polarly magnetic.

A treatment of the mineral with 0.1 *N* HCl does not affect its magnetic properties. In reliefless thin-sections of gold particles prepared with the aid of A. P. Perelyaev, no foreign inclusions have been discovered; upon being tested with a CrO_3 solution in HCl, the thin peripheral parts of the gold particles were found but very slightly etched, *i. e.* they are high-grade. The internal ground mass of the gold particles is etched rather vigorously, to a greater extent than in common gold. This points to magnetic properties being constitutional in the mineral.

In order to give a quantitative characteristic of the magnetic properties of the gold described, we undertook to determine its voluminal magnetic susceptibi-

lity; test was carried out by T. N. Rose by the induction method at the electromagnetic laboratory of the Sverdlovsk Affiliated Branch of the All-Union Scientific Research Institute of Metrology. In the course of a determination of the degree of magnetization of the specimen, made in a magnetic field with a density of 440 oersteds, the natural magnetic remanence was not separated from the induced magnetism.

The volume magnetic susceptibility was found to be

$$\varkappa = 0.040 \text{ CGS } \mu_0 \pm 0.005 \text{ CGS } \mu_0$$

The value obtained characterizes the native gold investigated as a ferromagnetic substance. Among natural minerals there are but very few that possess ferromagnetic properties. According to its volume magnetic susceptibility, native gold occupies among those minerals an intermediate place: its value of $\varkappa$ is lower than that of magnetite and pyrrhotite, but higher than that of common hematite and ilmenite [after J. Koenigsberger (3)].

Minerals	$\varkappa$
Magnetite	0.70—1.22
Pyrrhotite	0.055
Native magnetic gold	0.040
Ilmenite	0.004—0.007
Hematite	0 001—0.022

Thus, the discovery of native magnetic gold increases the list of strongly magnetic minerals.

The causes of the outstanding magnetic properties of the gold here described should be sought for in its peculiar chemical composition. A quantitative analysis of the mineral, carried out with great care by K. A. Nenadkevich at the Institute of Geological Sciences of the Academy of Sciences, yielded the following results:

Au	78.24 per cent
Ag	17.33 » »
Fe	4.4 » »
Total	99.97 » »
Sp. gravity	15.54

In the course of his spectroscopic study of the specimen N. V. Lizunov discovered in addition medium lines of Cu, weak lines of Ni, Bi and Mn, very weak lines of Ca and Si, and traces of Pb, Sn, Co, Al and Mg lines.

From the quantitatively determinable constituents of the mineral, Au and Ag are by themselves diamagnetic substances ($\varkappa$ is equal to 0.0000029 and 0.000002, respectively (2)), and the magnetic properties are undoubtedly due to the presence of Fe.

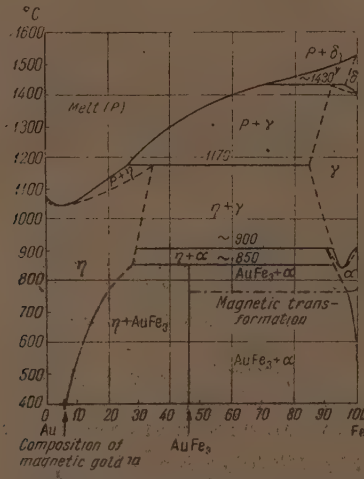
Some experimental data concerning the influence of Fe upon the magnetic properties of the gold are given by Shih (4). He has shown that ferromagnetic properties appear in artificial alloys of Au and Fe when the Fe content attains over 5 and up to 10 per cent. According to the constitution of the Au—Fe system (5), this boundary of the Fe admixture corresponds to a transition from the region of a solid solution of Au and Fe to alloys with a content of a new phase of $AuFe_3$. According to its Fe content, the native magnetic gold here described closely approaches the corresponding ferromagnetic alloys of Shih, also fitting within the boundary region* (see figure); the appearance of a certain amount of the $AuFe_3$ compound in a form apparently inaccessible to microscopic diagnostics is therefore possible in this native gold too, along with a solid solution of Au—Ag—Fe**. The question naturally arises whether the ferromagnetism of artificial iron-gold

* At a normal temperature the region of the solid solution should be narrower.

** Evidently, it is with the entrance of Fe into the solid solution that the above-mentioned comparatively easy etching of the gold with a chromium trioxide solution is associated.

alloys and native magnetic gold is not related with the appearance of a new phase of $AuFe_3$. In order to settle this question new experimental work is required.

The discovery of native undoubtedly magnetic gold makes it advisable carefully to test gold for its magnetic properties, iron being a quite frequent admixture to its chemical composition. In the latter respect iron ranks second, usually occurring in gold in lesser quantities than silver, but in larger amounts than copper (leaving aside cuprous gold); a Fe content of gold equal to 3—4 per cent, according to new



Au—Fe system, according to Hansen [5]. Composition of native magnetic gold according to Fe content denoted by a cross on the abscissae

data by Plaksin and Nasluzov [6] is not infrequent, *e. g.* for the deposits of the Urals and Kolyma. The possible magnetic properties of native gold should sometimes be taken into consideration also while carrying on magnetometric prospecting of gold-bearing quartz veins [7].

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GENETICS

ON SEX DIFFERENCES IN SUSCEPTIBILITY OF IMAGINAL DISCS IN *DROSOPHILA MELANOGASTER* LARVAE TO NOXIOUS AGENTS

By P. G. SVETLOV and O. V. CHEKANOVSKAYA

(Communicated by A. A. Zavarzin, Member of the Academy, 9. VI. 1944)

New experiments ([1],[2]) on the susceptibility of larvae and pupae demonstrated that the larvae just before the pupation show no signs of any sex difference in their susceptibility to lethal doses of ether. At the earliest stage of pupation, however (white pupae at an age of no more than 2 hours after pupation), the differences become quite manifest and continue to increase according as the pupae grow older. The existence of sex differential of susceptibility at so early a stage of pupation can scarcely be accounted for by anything else than by the differences in the susceptibility of imaginal primordia. But as at this stage of development there are no sharp morphological distinctions between the imaginal anlages and the corresponding anlages of the larva, we were brought to assume that the sex differences in the susceptibility of the embryonic cells of imaginal discs may already be present in larvae, though masked in them by a similar susceptibility of the cells of the larval tissue in both sexes.

In order to check up this assumption we undertook experiments that had to determine the susceptibility of imaginal discs in larvae. There exist several methods for testing tissue susceptibility. The most accurate among them are such as involve vital staining with a subsequent application of a dark field condensor (ultramicroscopy). It was this method that we applied to imaginal discs of *Drosophila*. The imaginal discs were prepared for the experiments under a binocular magnifying glass in a salt solution according to Ephroussi and Beadl (1936) (NaCl, 7.5; KCl, 0.35; $CaCl_2$, 0.21 per one litre of water).

Imaginal discs of the second pair of legs were always used. When examined in the dark field, in the saline, injured discs were invariably found to display a certain luminescence effect. Their cells contain fat-like inclusions in the form of a few granules; if high magnification is applied, it becomes apparent that only these granules emit light in the dark field, while the rest of the components of the cell are optically void. If examined under lower magnification, intact imaginal discs display a typical picture of uneven weak luminescence of a somewhat yellowish hue. At those points only where the trauma cannot possibly be avoided (the foot of the disc and the points of the trachea entrance, which are cut during preparation) a bright white opalescence is observable, sharply demarcated by the area of injury. Upon immersion into toxic liquids all the cells of the imaginal discs begin to opalesce after some time or other, and the whole disc begins to emit then an even white light, occasionally of a bluish hue. It is beyond any doubt that this picture testifies to the coagulation of proteins and to necrotic phenomena. If imaginal discs previously stained with neutral red are immersed into toxic solutions, one becomes easily convinced that the appearance of the bright white opalescence nearly coincides in time with the appearance in the cells of the well-known Nassonov phenomenon which consists in the absorption of vital stain by the

nuclear components. It is therefore not excluded that the phenomenon of paranecrosis observed in our experiments may serve as a criterion of cell injury. But the problem of reversibility of the phenomena obtained by us in the dark field being out of the scope of this investigation, we do not feel quite sure of it.

As material for our experiments served larvae ready for pupation, larvae 3 mm long (2-day-old), and larvae 4 mm long (3-day-old). The sizes of imaginal discs of legs in 3 mm larvae average 150×75 μ. This is the minimum size of discs that could be severed from the larvae without traumatizing them. The results of the experiments are summarized in Table 1. The sex of the larvae was determined before the experiment, according to the sizes of the sex anlages.

The noxious agents proved not all equally suitable to these experiments. With distilled water, hypotonic solutions, alcohol, ether and formalin we failed to observe in the dark field such picture as would permit precisely to record the setting-in of a definite effect. Neither was it possible to avoid any personal judgment in the interpretation of the pictures observed. Unlike this, the solutions of lactic acid and corrosive sublimate proved extremely suitable to the purpose. In this case the process of traumatization was accompanied with phenomena so distinct that no difficulties whatever were involved in the observation of similar effects and in recording the moments of its appearance with an accuracy of 1 minute.

Table 1

Material: imaginal discs of 2nd pair of legs	Noxious agent	Males		Females	
		Number of exper.	Mean time necessary to necrotic phenomena to set in, $M \pm m$ (min.)	Number of exper.	Mean time necessary to necrotic phenomena to set in, $M \pm m$ (min.)
Larvae ready for pupation	Lactic acid 0.007%	28	8.60±0.64	32	15.81±1.33
Do	Sublimate 0.002%	7	13.4	7	20.2
Larvae 4 mm long	Lactic acid 0.014%	16	3.72±0.04	16	7.0±0.10
Larvae 3 mm long	Do	16	3.75±0.25	16	8.03±0.42

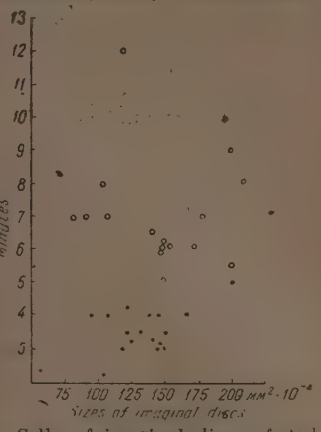
As may be inferred from Table 1, the susceptibility of the cells of imaginal discs is much higher in males than in females. The difference between the average terms of the appearance of necrotic phenomena everywhere exceeds the mean error of difference (m_{diff}) 4—10 times (for lack of space the errors of difference are omitted here). In larvae ready for pupation the extreme variants of susceptibility do somewhat overlap one another, while in young larvae the difference in the susceptibilities in males and females is so important that there is scarcely any transgression in the extreme variations.

The experiments with sublimate were undertaken with the purpose to satisfy oneself that the effects obtained in the dark field are no specific response of the plasm to lactic acid. The results went to demonstrate with sufficient clarity that the susceptibility to any other toxic solution of absolutely different chemical or pharmacological nature obeys exactly the same relation between the two sexes. This is suggestive of the assumption that the effect of luminescence in the dark field actually testifies to a primary susceptibility of the cells of imaginal discs.

Measurements of the discs have shown their sizes in females somewhat to exceed those in males of a similar age. Thus, it still appeared possible that the differences between the variations in the terms of the effect of the noxious substances upon the embryonic cells in males or females were due to the sizes of their respective imaginal discs. However, in the case of a correlation between the size of imaginal discs and their susceptibility, this correlation would hold within the limits of either sex, as well. As a matter of fact, correlation curves plotted with the

aim to check up this assumption failed to bear out any such correlation. One of these curves plotted for larvae 4 mm long is given in the figure. There is no trace of rectilinear distribution of points either in males or females; thus, no correlation between the sizes of imaginal discs and their susceptibilities could be recorded. What is clearly borne out by the plot is a greater susceptibility of the embryonic elements in males, as compared to those in females.

Next we endeavoured to determine the susceptibility of the tissues of various larval organs. Under experiment were the salivary glands and the piloric appendages of the stomach. The material was treated according to the method here described with lactic acid and corrosive sublimate, and the effect produced was observed under the microscope in the dark field. The examination revealed no signs of any difference between the susceptibility of larval tissues in males and females. Numerical data on the effect of lactic acid, 0.014 per cent strong, upon the proximal regions of salivary glands of larvae ready for pupation are given in Table 2. Table 2 shows the terms of appearance of necrotic phenomena in the dark field to coincide in both sexes with an accuracy of up to 0.05 minute. The differences between the means are much smaller than the difference error. The susceptibility of the larval tissue may thus be regarded as being equal in either sex. This should evidently been taken to account for the equal susceptibility in both sexes of intact larvae recorded in our previous communication (2).



Cells of imaginal discs of 2nd pair of legs in a *Drosophila melanogaster* larva (4 mm long) as affected by lactic acid. Denotation: points—males, circles —females

Table 2

Males			Females		
Number of exper.	Extreme variants (min.)	Mean values $M \pm m$ (min.)	Number of exper.	Extreme variants (min.)	Mean values $M \pm m$ (min.)
19	7—18	11.63±0.65	19	9—15	11.63±0.58

The sex differential of susceptibility is established only in the embryonic cells of imaginal discs; it has also been observed by the author in pupae, when examined in an analogous way in the dark field. The result of these experiments will be described at some later date.

The discovery of a sex differential of susceptibility in young larvae makes us view the ontogenesis of this phenomenon at a different angle. Its origin should apparently be looked for at earlier developmental stages. The possibility is not excluded that an egg already displays sex differences of susceptibility, which are preserved by embryonic cells serving to build up the imaginal organs, but become obliterated in larval tissues.

It may thus be considered as safely established that: 1) the origin of sex differential in the ontogenesis is traceable to the earliest larval stages; and 2) sex differences in susceptibility are based upon differences in the plasmic susceptibility.

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PLANT PHYSIOLOGY

CHEMICAL CHANGES OCCURRING IN ROOTS OF KOK-SAGHYZ DURING SUMMER PAUSE

By S. M. MASHTAKOV

(Communicated by A. A. Richter, Member of the Academy, 29. V. 1944)

The summer pause, or the summer period of rest in kok-saghyz sets in mostly on the second year of life. It is expressed at first in the yellowing and drying of the external leaves, and later on of the whole rosette. The lack of photosynthetic activity during the period of rest which, according to the external conditions, may last from several days to two months or more, leads to a reduction in the weight of the organic mass of the plants.

Qualitative studies of the changes occurring during the rest in the substances contained in the roots are of considerable interest, for they contribute to the solution of the problem on the rôle played by rubber in the plant's life, a divergence of opinion still existing upon this point.

Up to the present day there is no accord among the students even on the variation of rubber content in the roots of kok-saghyz during the active growth of the plant. However, taking into account the facts [1, 2, 6, 7, 9, 11] and the degree of precision of the methods employed, the formation and polymerization of rubber in growing living healthy roots of kok-saghyz are likely to be irreversible processes. It is of interest, therefore, to study the quantitative variation of the rubber during the summer pause as compared with that of other chemical components whose physiological rôle is already known.

The question as to the chemical changes occurring in the roots of kok-saghyz during the summer pause has not been sufficiently treated in literature. And the scarce evidence available refers to quantitative changes in rubber content only, while scarcely any mention of other substances is to be found; but the evidence available cannot be considered conclusive either, since the analysis of the roots was made without previous removal of the «case».

It is well known that the root cortex of the previous year is separated by a cork layer forming the so-called «case» [12]. The «case» which is isolated from the young growing tissues, has no connexion with the living organism of the plant. Our studies have shown [8] that the chemical changes taking place in it follow an entirely different course and are governed by other laws than in the new growing cortical tissues of the root.

The data reported below were obtained from an analysis of the roots of kok-saghyz under the removal of the «case». Observations were made in the Moscow region during the 1938 season which was distinguished by a great drought. The duration of the summer rest of the plants exceeded two months. The roots to be analysed for rubber, resins, nitrogenous materials and carbohydrates were taken at a solid plot at the following three dates: 1°, at the beginning of the full rest (27.VII); 2°, at the beginning of secondary growth (4.X); 3°, at the period of secondary growth (27.X).

The results of the analysis are summarized in Tables 1 and 2.

The data contained in Table 1 show that during the period of full rest there is an increase in percentages of rubber, resins, monosaccharides and of the total

Table 1

Content of Substances in the New Tissue of Kok-saghyz Roots in % («case» removed)

	Beginning of rest	End of rest	Secondary growth
Rubber	5.40	6.12	7.16
Resins	2.02	2.16	8.42
Monosaccharides	3.79	5.59	8.26
Inulin	54.72	45.07	40.95
Nitrogen total	2.78	3.12	3.12
» soluble	1.95	2.48	2.54
» proteinic	0.83	0.65	0.64

and soluble nitrogen. On the other hand, the percentages of inulin and of proteinic nitrogen decrease. The percentage of inulin decreases continually at the beginning of the secondary growth when the new leaf rosettes are formed (from 4.X to 27.X). On the other hand, the percentage of rubber, resins and monosaccharides is continually increasing during the same period, while the percentage of nitrogenous materials remains nearly constant.

The absolute quantities of the majority of the materials referred to above vary in a somewhat different way (Table 2).

Table 2

Absolute Content of Substances in New Tissues of Kok-saghyz Roots (gs pro 100 roots)

	Beginning of rest	End of rest	Secondary growth
Dry weight of the roots	168	145	141
Rubber	9.07	8.87	10.10
Resins	3.39	3.13	3.41
Monosaccharides	6.37	8.11	11.65
Inulin	91.93	65 35	57.74
Nitrogen, total	4.67	4.63	4.48
» soluble	3.28	3.69	3.58
» proteinic	1.39	0.94	0.90

It may be inferred from Table 2 that there is a general decrease in the dry weight of the roots, while the quantity of rubber remains constant during the whole period of rest. There is an increase in rubber content only during the period of secondary growth. Towards the end of the rest there is a certain decrease in resins, but it is restored after the beginning of the secondary growth of the plants. The quantity of total nitrogen does not change towards the end of the period of rest; the soluble nitrogen increases, while the proteinic nitrogen suffers a sharp drop. Similarly there is a sharp decrease in the absolute content of inulin, while that of monosaccharides is considerably increased. In Table 3 is presented the content of substances towards the second and third dates, as compared with the original content (at the beginning of rest) put at 100.

The results thus obtained make one conclude that during the summer rest of kok-saghyz under the complete absence of photosynthetic processes, a strong hydrolysis of inulin and proteins takes place in the roots; the living tissues of the roots are thus enriched in monosaccharides and soluble nitrogen. As the quantity of total nitrogen remains constant while the total carbohydrates become considerably reduced, one may conclude that the decrease in the dry weight of the root of kok-saghyz during the summer rest is due to a reduction of the carbohydrates (mostly of inulin) which are spent on respiration. After the rest is over, at the time of secondary growth, the decrease in the quantity of the carbohydrates and of the nitrogenous materials is going on, which may be explained by a partial migration

Table 3

	Dry weight of the roots	Inulin	Monosaccharides	Total carbohydrates	Nitrogen: proteinic	Nitrogen: soluble	Nitrogen: total	Resins	Rubber
Beginning of full rest (27. VII)	100	100	100	100	100	100	100	100	10
End of rest, beginning of the growth (4. X)	86	71	127	75	68	112	99	92	98
Period of the secondary growth (27. X)	84	63	183	70	65	109	95	101	111

of these materials from the roots to the aboveground organs and by their consumption in connexion with the formation of new leaves.

The absolute rubber content in the roots remains constant throughout the period of rest. This fact proving that the amount of rubber contained in the roots is not reduced during the period of rest (as compared with a sharp reduction of the quantity of the carbohydrates and proteins) is in a sharp conflict with the theory that rubber belongs to reserve materials ([5], [13], [14]).

On the other hand, the same fact shows that the lack of growth processes during the period of rest leads to a full arrest of rubber synthesis, so that the amount of rubber does not increase during the same period. Isolated contrary statements still appearing now and pretending to prove the fact of an increase of the amount of rubber during the summer rest ([10]), are due to misunderstanding and have no ground whatever. As shown by the above tables, rubber synthesis is resumed only after the rest is over and secondary growth processes take place. Even the accumulation of rubber in the roots of kok-saghyz during the period of their storage in piles is directly connected with the growth processes, since storage results in growth of the majority of the roots owing to their great regeneration capacity.

These growth processes which take place in plants apt to regeneration, lead to a change in the direction of the internal biochemical reactions ([3], [8], [15]) resulting in an accumulation of the products of incomplete oxidation and reduction. All this goes to support the view that the formation and polymerization of rubber takes place in living healthy roots at the period of growth only.

Full arrest of growth, for example, during the summer rest, leads to a stabilization of the amount of rubber. A breakdown of rubber and a decrease in its amount takes place only in dying tissues of kok-saghyz, as shown by us in the process of «case» formation ([9]) or in dead roots of kok-saghyz during their storage in piles ([10]).

Conclusions. The period of summer rest leads to a reduction of the total organic mass of the roots of kok-saghyz, mainly at the expense of carbohydrates; during the period of rest an intense hydrolysis of inulin and proteinic substances is observed; the amount of rubber remains constant. Synthesis and accumulation of rubber in the roots of kok-saghyz are resumed only during the secondary growth processes, when the pause is over.

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PLANT PHYSIOLOGY

CO_2 ASSIMILATION IN GROWING ORGANS

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It has been shown in recent studies by Richter, Sukhorukov and Ostapenko ([1], [2]) that there is no functional connexion between growth, accumulation of matter and assimilation power of the green leaf. It has likewise been proved ([3]) that the stages of development do not affect carbon dioxide assimilation either. The studies referred to above went to establish the constancy of photosynthesis in a fully developed leaf, and a certain autonomy of the chloroplasts as regards their function.

During the growth of a cell of the assimilative tissue, the chloroplasts also pass, along with other constituents of the cell, a development of their own, although this process is far from being cleared up ([4]). There could be consequently anticipated a complex relation between the photosynthesis and the growth of the plant as a whole, an organ, a cell and of the development of chloroplasts.

In order to clear up these relations we have studied photosynthesis in the growing plants of *Helianthus annuus*. The plants were grown at the experimental plot of the laboratory until they developed six pairs of leaves. Some of the plants were decapitated in order to modify the rate of growth. The reaction to decapitation became patent on the second day and consisted in the hyponasty of the upper leaves; after three days there took place a change in the angle of deflection of the petioles from the perpendicular to the stem (Table 1).

The results of measurements of the areas of leaf-blades in normal and decapitated plants are given in Table 1. Determination of photosynthesis was made after Warburg, the conditions being the same as described by Richter, Sukhorukov and Ostapenko ([1]).

Table 1

Plant	Position of leaf	Leaf area in cm²			Increment of area after 6 days	Increment of area in %	Mgs CO_2 per hour pro dcm²				Angle, sec.
							23.IX		26.IX		
		20.IX	23.IX	26.IX			photo-synthe-sis	respi-ration	photo-synthe-sis	respi-ration	
Normal	Next to cotyledons	40.03	40.43	40.47	0.40	0.99	10.50	2.22	8.84	1.91	15
	2 pair	78.53	80.14	85.74	7.21	9.30	8.04	1.47	8.33	1.76	30
	3 »	88.55	88.55	123.09	34.54	40.13	9.21	2.23	12.15	2.45	45
	4 »	26.39	37.76	44.39	18.09	68.78	12.15	4.00	—	—	70
	5 »	4.02	8.77	13.27	9.25	230.09	—	—	—	—	70
Decapitated	Next to cotyledons	31.05	42.83	46.24	15.19	48.92	8.80	2.04	8.66	1.91	10
	2 pair	70.65	94.19	106.54	35.89	50.72	8.59	1.94	9.10	2.39	30
	3 »	108.13	125.60	157.98	49.85	46.10	9.17	2.21	10.75	2.63	50
	4 »	33.36	50.76	90.08	56.72	170.02	9.99	3.22	—	—	75
	5 »	8.48	14.13	37.44	28.96	341.74	—	—	—	—	90

A comparison of the increment of the area of leaf-blade with the intensity of photosynthesis shows that there is no obvious relation between growth and photo-

synthesis. The growth of the leaf-blade in decapitated plants is more rapid; at the same time, CO_2 assimilation (*i. e.* photosynthesis minus respiration) proceeds at the same rate in all leaves.

Table 2 contains data on the increment of the stem and photosynthesis at different levels. For determining photosynthesis portions of the stem were diametrically bisected lengthwise, and photosynthesis was determined with the aid of the usual method. Calculations were made for the area of the lateral surface of the cylinder.

Table 2

Plant	Internode	Increment after 6 days in mm	Increment in %	Mgs CO_2 per hour pro dcm²			
				23.IX		26.IX	
				photosynthesis	respiration	photosynthesis	respiration
Normal	Hypocotyl	0	0	7.04	6.11	9.82	7.98
	2nd internode	0	0	5.73	5.36	7.95	6.89
	3 »	19	17.92	—	—	8.27	6.94
	4 »	35	140.00	9.69	9.47	12.58	9.62
	5 »	24	240.00	—	—	—	—
	6 »	10	200.00	—	—	—	—
Decapitated	Hypocotyl	0	0	5.95	5.76	15.40	10.82
	2nd internode	0	0	3.66	3.29	8.57	7.57
	3 »	10	12.50	6.27	5.57	8.86	7.79
	4 »	25	100.00	—	—	12.82	10.34
	5 »	28	280.00	—	—	—	—

The figures presented above show that CO_2 absorption by the stem in light is insignificant, photosynthesis taking place mainly at the expense of the carbon dioxide of respiration. A certain parallelism between respiration and photosynthesis is observed. Anatomical examination of the stem shows that the chloroplasts are located chiefly in the external layers of the cortical parenchyme, they are also contained in the epidermis and in the multicellular basal portions of the living trichomes, outgrowths of the epidermis. The stomata are rare in the epidermis, the latter being covered with cuticle. In the external layers of the cortical parenchyme there are well developed intercellular spaces. As may be seen, the structure of the young stem is favourable for the assimilation of the carbon dioxide of respiration and is but little favourable for the assimilation of atmospheric carbon dioxide (cuticle, scarce stomata).

In order to check up this point, determination of photosynthesis was made in stem segments at varying CO_2 concentrations. No increase in photosynthesis was observed.

Stems: 3rd internode, 0.206 per cent CO_2; photosynthesis, 8.27; 1 per cent, 8.47 mg CO_2 per hour pro dcm².

Stems: 4th internode, 0.206 per cent CO_2; photosynthesis, 12.58; 1 per cent, 10.14 mg CO_2 per hour pro dcm².

The studies here reported make us conclude that a certain level of photosynthesis is established in the growing leaf at a rather early stage; other processes taking place in the same organ do but slightly affect it.

There is a relation between photosynthesis and respiration in the stem. The nature of this relation consists in the enrichment of the intercellular spaces with carbon dioxide formed by respiration; respiration becomes in this instance an external agent of photosynthesis.

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